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CASTING OF HALIDE AND FLUORIDE  
ALLOYS FOR LASER WINDOWS

R. T. Newberg, et al

Raytheon Company

Prepared for:

Air Force Cambridge Research Laboratories  
Defense Advanced Research Projects Agency

15 April 1975

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CASTING OF HALIDE AND FLUORIDE  
ALLOYS FOR LASER WINDOWS

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Raytheon Research Division  
Waltham, Massachusetts 02154

15 April 1975

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Abstract (Cont'd.)

ingots cast from single crystal chips and pre-treated powder, respectively. Strained ingots of  $\text{CaF}_2$  were successfully strain annealed at  $900^\circ\text{C}$  either in a vacuum or in an inert atmosphere. Strained ingots of  $\text{SrF}_2$  were successfully strain annealed at  $1000^\circ\text{C}$  in a high vacuum.

Preliminary mechanical measurements on cast and single crystal  $\text{CaF}_2$  and cast and single crystal  $\text{SrF}_2$  show average fracture strengths ranging from 8000 psi to 28,200 psi, from 7200 psi to 26,500 psi, from 10,800 psi to 16,000 psi, and from 11,300 psi to 16,400 psi, respectively, depending both on the quality of polished surfaces and edges and on whether or not the polished samples are annealed prior to testing. This dependence is evidence that the fracture strength is limited by surface and/or edge flaws. The preliminary results show the equivalence in strength of  $\text{CaF}_2$  and  $\text{SrF}_2$  and of polycrystalline cast and single crystal material.

## TECHNICAL PROGRAM SUMMARY

The main objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for high power laser window applications. The main effort deals with the fabrication and property evaluation of the alkaline earth fluorides.

During the second six months of this program high quality castings of both  $\text{CaF}_2$  and  $\text{SrF}_2$  were fabricated, regardless of the starting material. That is, either high purity single crystal chips or pre-treated "reagent" grade powder can be used as starting material to yield equivalently cast ingots.

Castings of  $\text{CaF}_2$  were attempted in an inert atmosphere of purified argon (1-50 torr). The advantage over vacuum casting is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas.

Preliminary hot forgings of polycrystalline cast  $\text{CaF}_2$  were done at 1000°C. At the high temperature a large grain size results so that not much advantage in grain size reduction is gained.

Calorimetrically measured  $5.25\mu\text{m}$  bulk absorption coefficients for cast  $\text{CaF}_2$  are being consistently attained near  $4.2 \times 10^{-4} \text{ cm}^{-1}$  regardless of the starting material. Those castings of  $\text{CaF}_2$  fabricated in an inert atmosphere (purified argon) have  $5.25\mu\text{m}$  apparent absorption coefficients typically greater than  $1 \times 10^{-3} \text{ cm}^{-1}$ , although one excellent casting was obtained ( $4.1 \times 10^{-4} \text{ cm}^{-1}$ ).

In preliminary results the  $5.25\mu\text{m}$  bulk absorption coefficient of cast  $\text{SrF}_2$  lies near  $6.7 \times 10^{-5} \text{ cm}^{-1}$  for an ingot using single crystal chips as starting material and lies near  $1.7 \times 10^{-4} \text{ cm}^{-1}$  for an ingot cast from purified "reagent" grade powder.

Strain annealing of highly strained cast  $\text{CaF}_2$  has been successful at

900°C either in a vacuum or in an inert atmosphere. Similarly strained ingots of cast  $\text{SrF}_2$  have been successfully strain annealed at 1000°C, but only in a high vacuum furnace.

Mechanical measurements on cast  $\text{CaF}_2$  show average fracture strengths ranging from a minimum near 8000 psi to near 28,200 psi, depending on both the quality of polished surfaces and whether or not the polished samples are annealed at 900°C (a strain relief procedure) prior to testing. The values are equivalent to the values obtained for single crystal  $\text{CaF}_2$  for which similar polishing and annealing procedures show average fracture strengths ranging from 7200 psi to 26,500 psi. In preliminary results, the average fracture strengths for cast and single crystal  $\text{SrF}_2$  range from 10,800 psi to 16,000 psi and from 11,300 psi to 16,400 psi, respectively. The best (for  $\text{CaF}_2$ ) surface polish has not yet been evaluated for  $\text{SrF}_2$ , but these results show that for both  $\text{CaF}_2$  and  $\text{SrF}_2$  the dependence of fracture strength on both surface polish and annealing history is evidence that fracture may be determined by surface and/or edge flaws. The preliminary results also show that  $\text{SrF}_2$  is equivalent in strength to  $\text{CaF}_2$  and that polycrystalline cast material is equivalent in strength to single crystal material.

## PREFACE

This report was prepared by Raytheon Company, Research Division, Waltham, Massachusetts under Contract No. F19628-74-C-0148 entitled "Casting of Halide and Fluoride Alloys for Laser Windows." This work is supported by the Advanced Research Projects Agency and is monitored by the Air Force Cambridge Research Laboratories, Bedford, Massachusetts.

At Raytheon the investigation is being carried out in the Advanced Materials Department under the direction of Dr. J. Pappis, principal investigator, and Dr. R. Newberg. Assisting with material fabrication and processing are T. Wong and A. De. Optical polishing is provided by R. Cosgro; Dr. T. Kohane and T. Varitimos are performing the laser calorimetry measurements. Dr. O. Guentert, W. Tye, and D. Howe are providing the SEM micrographs, microprobe analyses, and X-ray diffraction analyses. P. Roman is assisting with the mechanical property measurements. This report has been given an internal number of S-1864.

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## 1.0 INTRODUCTION

The primary objective of this program is to demonstrate the feasibility of fusion casting of alkali halides and alkaline earth fluorides for use as windows for high power lasers. In a previous program, initial work on alkali halide alloys, particularly  $\text{SrCl}_2$ -doped KCl, indicated that casting was a promising fabrication process.

The work on the alkaline earth fluorides is being stressed because they are more amenable to fabrication by fusion casting due to their smaller volume change on solidification and their better thermal and mechanical properties compared to the alkali halides, as was discussed in a previous report.<sup>1</sup> Therefore, this program investigates the effects of casting parameters and annealing procedures on the microstructure, mechanical properties, and optical properties of the alkaline earth fluorides. In addition, the effects of impurities and alloy additions on microstructure and properties are being evaluated. Equally significant is the study of the importance of starting materials and purification schemes on the optical absorption and scatter of the cast ingots.

## 2.0 RESULTS

### 2.1 Vacuum Casting

During the second six months of this program, the main effort was directed toward the fusion casting of pure alkaline earth fluorides, with most emphasis having been placed on  $\text{SrF}_2$ . Both large vacuum furnaces were used, with most of the casting (92 runs) having been done in the vacuum hot press (VHP) furnace capable of ingots of about five and one-half inches in diameter. The two-zone (CF) furnace was used for casting (11 runs), annealing (35 runs) and purification of "reagent" grade powder (17 runs). Two hot forging runs and two purification runs were also done in the VHP furnace.

Tables I and II list all the runs done in the two furnaces. Figures 1 and 2 show several polished windows of pure  $\text{CaF}_2$  and  $\text{SrF}_2$ , respectively, cast in the laboratory. The grain size of such castings is large - typically on the order of 1 - 2 cm.

As mentioned above, nearly all of the castings were produced in the VHP furnace (an all graphite system). During the third quarter, six runs (CF91 - 96) were attempted in the two-zone furnace as listed in Table II. Earlier in this furnace, as was discussed in a previous report,<sup>1</sup> there had been a problem with the reaction of fluoride vapors with the insulating supports for the molybdenum elements and with the thermocouple insulating tubes. However, these six runs demonstrated that the problem is associated only with  $\text{CaF}_2$  and not with  $\text{SrF}_2$ ; i.e., with the present castings of  $\text{SrF}_2$  no such reactions occurred up to 1500°C. The castings were generally discolored, probably a result of the poor vacuum (1 - 10 $\mu\text{m}$ ) capability provided by the mechanical pump vacuum system. A diffusion pump was installed late in this reporting period providing vacuum capability of at least  $10^{-5}$  torr. Five initial casting runs (CF 126-130) were attempted using  $\text{SrF}_2$ . Transparent material with no discolorations was obtained but cooling procedures to promote unidirectional solidification still need to be improved.

TABLE I  
VACUUM HOT PRESS (VHP) RUNS  
PURE FLUORIDES

<u>VHP No.</u>	<u>Material</u>	<u>Comments</u>
284, 285	$\text{SrF}_2$	Small castings; cracked
286-297	$\text{CaF}_2$	Large castings; good runs
300	$\text{SrF}_2$	Large casting; cracked
301	$\text{CaF}_2$	In argon 50 mm; colorless casting
302, 303	$\text{CaF}_2$	Hot forged samples (VHP-269) at 1000°C
304	$\text{CaF}_2$	In < 1mm argon; bluish casting
306	$\text{CaF}_2$	In 5 mm argon; yellowish casting
307, 308, 309	$\text{CaF}_2$	From purified powder; castings cracked
311, 312	$\text{SrF}_2$	Fast cooled; castings cracked
313	$\text{CaF}_2$	In 15 mm argon; bluish casting
314	$\text{CaF}_2$	In 50 mm argon; yellowish casting
316	$\text{CaF}_2$	Small casting; intergranular cracks
317	$\text{CaF}_2$	Remelt VHP-309; In 50 mm argon intergranular cracks; colorless casting
318	$\text{CaF}_2$	In 50 mm argon; no cracks; yellow-blue casting
319-321	$\text{SrF}_2$	Trouble with power supply; no melting
324	$\text{CaF}_2$	Purification of powder plus two percent teflon
325	$\text{SrF}_2$	Purification of powder plus two percent teflon
326, 327	$\text{SrF}_2$	Cooled nominal 75°C/ hr.; cracked
329	$\text{SrF}_2$	Melt VHP-325; cooled 45°C/ hr.; cracked cloudy ingot (white precipitates)
332	$\text{SrF}_2$	Remelt VHP-326; cooled 25°C/ hr.; good
333	$\text{CaF}_2$	Two crucibles in furnace; cooled 75°C/ hr.
334	$\text{SrF}_2$	Cooled 15°C/ hr.; no good
335	$\text{SrF}_2$	Purified powder (vacuum baked); cooled 25°C/ hr.; good
338	$\text{SrF}_2$	Cooled 25°C/ hr.; white precipitates
339	$\text{CaF}_2$	Not melted
340	$\text{SrF}_2$	Cooled 60°C/ hr.; good casting

TABLE I (Cont'd.)

341, 350	$\text{CaF}_2$	Cooled 75°C/ hr.; good
342	$\text{SrF}_2$	Cooled 75°C/ hr.; power failure; cracked
343	$\text{SrF}_2$	Remelt VHP-342; cooled 75°C/ hr.; good
344, 345	$\text{SrF}_2$	Cooled 75°C/ hr.; cracked
346	$\text{SrF}_2$	Cooled 45°C/ hr.; cracked
348, 349, 353	$\text{SrF}_2$	Cooled 35°C/ hr.; good
352	$\text{SrF}_2$	Cooled 20°C/ hr.; cracked
354	$\text{CaF}_2$	Cooled 35°C/ hr.; cracked
356	$\text{SrF}_2$	Cooled 35°C/ hr.; cracked
357	$\text{SrF}_2$	Purified powder (vacuum baked); cooled 75°C/ hr.; opaque
358	$\text{SrF}_2$	Remelt VHP-357; cooled 35°C/ hr.; cracked
360, 361	$\text{SrF}_2$	VHP-361 remelt of VHP-360, cooled 25°C/ hr.; good
363	$\text{SrF}_2$	Remelt VHP-358; not melted completely
364	$\text{SrF}_2$	Molybdenum crucible; cracked due to sticking
365	$\text{SrF}_2$	Cooled 25°C/ hr.; cracked
368	$\text{SrF}_2$	Too high temperature; melt evaporated
369, 370	$\text{SrF}_2$	VHP-370 remelt of VHP-369; cooled 35°C/ hr.; good
373, 374	$\text{SrF}_2$	Remelts; cooled 25°C/ hr.; no good
375	$\text{SrF}_2$	In 25 mm argon; thermocouple broke, power off; cracked
378-380		
382, 383	$\text{SrF}_2$	Remelts; no good
384	$\text{SrF}_2$	Remelt VHP-383; cooled 25°C/ hr.; good
387	$\text{CaF}_2$	Remelt crystals; manually cooled; cracked
388, 389, 393	$\text{SrF}_2$	Purified powder (teflon + roast); opaque, discolored; cracked
390	$\text{SrF}_2$	Purified powder (teflon + roast); cracked but transparent
394	$\text{SrF}_2$	Purified powder (teflon - no roast); cracked but clear
395	$\text{SrF}_2$	Remelt VHP-390 and VHP-394; cooled 35°C/ hr.; good
398	$\text{SrF}_2$	Remelt VHP-384; cooled 25°C/ hr.; good

TABLE I (Cont'd.)

399	$\text{SrF}_2$	Purified powder + remelt deposits, cooled $25^\circ\text{C}/\text{hr.}$ ; good
400, 402	$\text{SrF}_2$	Remelts of VHP-393 and VHP-399, cooled $25^\circ\text{C}/\text{hr.}$ ; good
403	$\text{CaF}_2$	Manually cooled; good
404	$\text{SrF}_2$	Remelt; cooled $25^\circ\text{C}/\text{hr.}$ , discolored (green); cracked
405, 409, 411	$\text{CaF}_2$	Purification with $\text{PbF}_2$
408	$\text{SrF}_2$	Remelt VHP-404; cooled $20-25^\circ\text{C}/\text{hr.}$ ; good
412	$\text{CaF}_2$	Remelt; manually cooled; no good

TABLE II  
TWO-ZONE FURNACE (CF) RUNS  
PURE FLUORIDES

<u>CF No.</u>	<u>Material</u>	<u>Comments</u>
70-77, 79-81, 83-85	$\text{CaF}_2$	Annealing (900°C) cast ingots
82, 88, 89, 97, 98	$\text{SrF}_2$	Annealing (900°C) cast ingots
78	$\text{CaF}_2$	Powder purification in teflon vapors (900°C)
86, 90	$\text{SrF}_2$	Powder purification in teflon vapors (900°C)
87	$\text{SrF}_2$	Vacuum bake powder (900°C)
91	$\text{SrF}_2$	Casting failed because it did not melt
92, 93	$\text{SrF}_2$	Casting in teflon vapor (partial pressure 50 - 100 $\mu\text{m}$ ). Ingots clear but cracked
94 - 96	$\text{SrF}_2$	Casting in teflon vapor (partial pressure 300 - 400 $\mu\text{m}$ ). Ingots discolored (pink) and cracked
97, 98, 100, 104 106, 107, 109, 110 113, 117-119	$\text{SrF}_2$	Annealing (900°C) cast ingots
99, 101-103	$\text{SrF}_2$	Vacuum bake powder (900°C)
105, 111, 112 114-116	$\text{CaF}_2$	Vacuum bake powder (900°C)
108, 122	$\text{SrF}_2$	Annealing (1000°C) cast ingots in teflon vapor (partial pressure 100 $\mu\text{m}$ )
121, 121a, 123	$\text{SrF}_2$	Powder purification in teflon vapor (100-200 $\mu\text{m}$ partial pressure) (600°C).
124, 125	$\text{SrF}_2$	Annealing (1000°C) in higher vacuum ( $10^{-4}$ - $10^{-5}$ torr)
126-130	$\text{SrF}_2$	Initial casting runs to test new vacuum system and Mo elements. Ingots transparent

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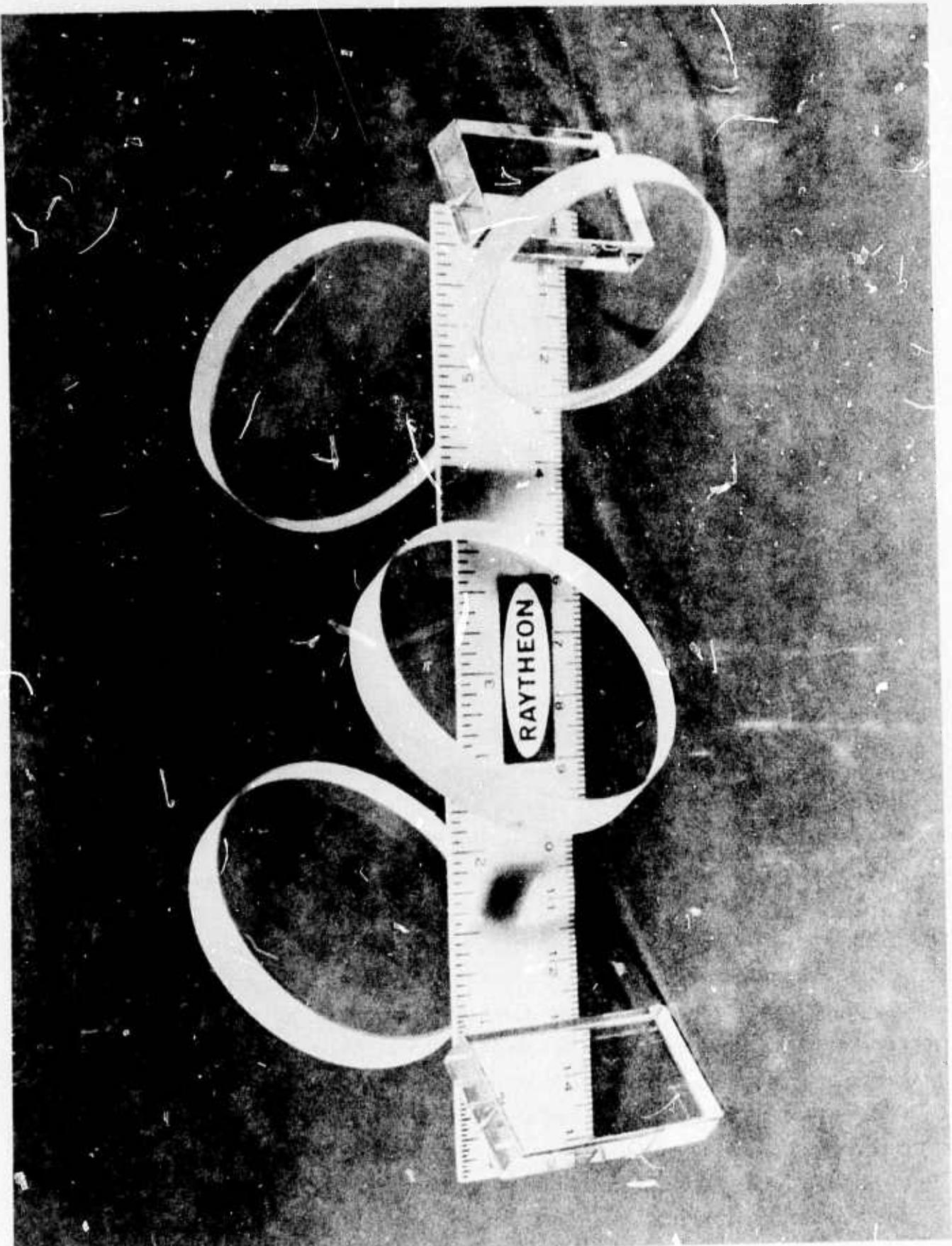
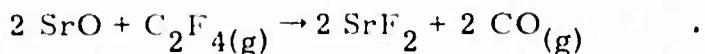
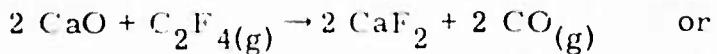


Fig. 2 Polished Windows of Cast SrF<sub>2</sub>

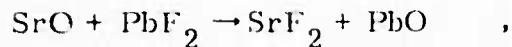
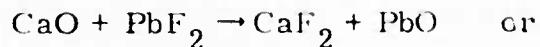
At the beginning of the casting program for  $\text{SrF}_2$ , it was noted that the cast ingots were more susceptible to cracking (probably from thermal shock) than were similar  $\text{CaF}_2$  ingots. The problem was in general remedied by modifying the VHP furnace to include temperature control over the entire range necessary (room temperature to over  $1500^\circ\text{C}$ ) as well as controlled cooling at rates as low as  $10^\circ\text{C}/\text{hr}$ . For casting  $\text{CaF}_2$  bare wire Pt; Pt-13percent Rh thermocouples can be used for temperature control, with an optical pyrometer being used as an auxiliary check of the temperature. For  $\text{SrF}_2$ , as mentioned above, alumina-sheathed Pt; Pt-13 percent Rh thermocouples can be used.

With such modifications, the present procedure for obtaining castings of  $\text{SrF}_2$  and  $\text{CaF}_2$  is as follows (for the vacuum hot press furnace): The charge to be melted (fluoride plus lead fluoride added as an oxide scavenger - usually 2 - 5 percent by weight) is loaded in a covered ATJ graphite crucible and placed in the furnace. The crucible rests on a PG (pyrolytic graphite) pedestal ("a" axis parallel to the desired direction of solidification) which in turn rests on the bottom water-cooled ram. A vacuum is drawn and, when it reaches  $10^{-4}$  torr, the furnace is brought slowly up to temperature in about three hours. The charge is held at  $1500^\circ\text{C}$  for one hour to insure complete melting. During this time the water-coolant to the bottom pedestal is turned off to maximize the temperature. In the final 15 minutes of melting, the water coolant is turned on to establish a thermal gradient in the crucible from top to bottom, in order to promote unidirectional solidification. The furnace is then switched to controlled cooling at the desired rate by adjusting the clock-drive controls. After complete solidification is assured, the water-coolant to the pedestal is again turned off to minimize the thermal gradient in the ingot, and the cooling rate may be reset to the desired cooling to room temperature. The total process requires about three days in the case of  $\text{SrF}_2$ .  $\text{CaF}_2$  can be cooled more quickly and the process requires only one day. All of the castings produced in the above manner are still quite strained (probably due to residual thermal gradients in the furnace). Consequently, each sample must be subsequently strain annealed in the two-zone vacuum furnace prior to further handling, as will be discussed below.

Starting material for most castings was high purity, single crystal chips of  $\text{CaF}_2$  (Optovac) or  $\text{SrF}_2$  (Harshaw). However, a number of castings of  $\text{CaF}_2$  and  $\text{SrF}_2$  were made from in-house purified "reagent" grade powder with equal success. As listed in Tables 1 and 2, several purification schemes were used. One has been discussed before,<sup>1</sup> using teflon vapors at elevated temperature according to the following thermodynamically favorable reactions:



The other procedure is to vacuum bake the "reagent" grade powder at  $900^\circ\text{C}$  to remove as much absorbed water as possible. The partially sintered powder can then be melted in the normal way with only lead fluoride being added as an oxide scavenger according to the reactions:



with the  $\text{PbO}$  and any excess  $\text{PbF}_2$  being removed by volatilization under vacuum at the elevated temperatures.

In purifying the "reagent" grade  $\text{SrF}_2$  powder (obtained from Barium and Chemicals, Inc., Steubenville, Ohio), both procedures were used. In using the teflon vapor technique at  $900^\circ\text{C}$  (CF-86 and 90), the teflon also pyrolyzes (as is the case with  $\text{CaF}_2$ <sup>1</sup>), and the resulting graphite contamination is difficult to remove by subsequent roasting in air at  $500^\circ\text{C}$ . The one casting (VHP-329) made from such powder was opaque (white precipitates), but upon subsequent remelting with additional lead fluoride added, transparent castings were obtained (VHP-346 and 349). Subsequent teflon vapor purifications were run at  $600^\circ\text{C}$  (CF-121, 121a, and 123) resulting in little or no pyrolysis with no obvious graphite contamination. Nonetheless several such purification runs were roasted in air ( $500^\circ\text{C}$ ) prior to casting with mixed results. One ingot

(VHP-388) was opaque and one (VHP-390) was clear. The former was remelted several times (VHP-389, 393, and 400) and was purified to transparency. However, the best results were obtained from the 600°C teflon-treated powder with no subsequent roasting. Two runs (VHP-394 and 399) produced clear castings.

In the purification scheme of the  $\text{SrF}_2$  powder, it was noticed that the as-received powder is contaminated with small black particles. The particles, being magnetic, are somewhat effectively removed by passing a magnet repeatedly through the powder. (X-ray diffraction and ion probe analysis show the contaminants to contain Fe - probably iron oxide due to the reddish brown colored powder obtained upon grinding - plus trace amounts of Al, Si, and Ti.) After such a mechanical separation some contamination remains because the vacuum-baked (or 600°C teflon-treated) powder is discolored pink. Mixed results were obtained in casting vacuum-baked powder (VHP-335 and 357), the ingots being clear and opaque, respectively. However, on remelting the opaque ingot, transparent ingots were subsequently cast (VHP-358 and 363).

Teflon-treated  $\text{CaF}_2$  (900°C) gives consistently good results (VHP-307, 308, 309, and 317).

It was at first noticed that castings produced from purified powder (both  $\text{SrF}_2$  and  $\text{CaF}_2$ ) seemed to be especially sensitive to intergranular cracking by thermal shock. It may have been due to trace residual impurities (e.g., residual Pb) at the grain boundaries with increased sensitivity to thermal shock, as will be discussed below. The problem was alleviated by using a crucible cover with a hole - the hole presumably allowing more volatile impurities to escape more readily. Subsequently some castings cracked but failure was predominantly transgranular in nature, i.e., cleavage across large grains.

Selected samples of "reagent" grade  $\text{CaF}_2$  and  $\text{SrF}_2$  were analyzed by emission spectroscopy (Jarrell-Ash, Waltham, Massachusetts). Table III shows the results of the analyses on the following  $\text{CaF}_2$  samples: 1) As-received "reagent" grade powder, 2) A casting (VHP-272) using teflon-treated powder, and 3) A casting (VHP-273) using untreated powder. As

**TABLE III**  
**ANALYSES OF "REAGENT" GRADE  $\text{CaF}_2$  SAMPLES**



**JARRELL-ASH DIVISION**

Fisher Scientific Company

**Certificate of Analysis**

TO: Raytheon Company DATE RECEIVED 10/17/74  
28 Seyon St. DATE REPORTED 10/28/74  
Waltham, MA 02154 ORDER NO. 90-77543  
ATTN: Mr. R. Newberg Mr. Swift

SAMPLE DESCRIPTION  $\text{CaF}_2$   
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

	1	2	3	1	2	3	1	2	3	1	2	3
U	ND	ND	ND	Zn	ND	ND	ND	ND	ND	Lu		
Be	ND	ND	ND	Ge	ND	ND	Te	ND	ND	Mt	ND	ND
B	ND	ND	ND	Ge	ND	ND	Ca	ND	ND	To	ND	ND
Na	800	ND	ND	As	ND	ND	Be	80	10	100	W	ND
Mg	10	5	10	Rb	ND	ND	La			Re	ND	ND
Al	.5	ND	1	Sr	400	400	600	Co		Os	ND	ND
Si	ND	ND	ND	V			Pr			Ir	ND	ND
K	ND	ND	ND	Zr	ND	ND	Nd			Pt	ND	ND
Ca	H	H	H	ND	ND	ND	Sn			Au	ND	ND
Ti	ND	ND	ND	Mo	ND	ND	Eu			Hg	ND	ND
V	ND	ND	ND	Ru	ND	ND	Gd			Tl	ND	ND
Cr	.5	ND	ND	Rh	ND	ND	Tb			Pd	ND	ND
Mn	2	ND	ND	Pd	ND	ND	Dy			Bi	ND	ND
Fe	5	ND	.1	Ag	ND	ND	Ho			Th		
Co	ND	ND	ND	Cd	ND	ND	Er			U		
Ni	ND	ND	ND	In	ND	ND	Tm			P	ND	ND
Cu	5	ND	ND	Sn	ND	ND	Yb			Se		

REMARKS  
1 =  $\text{CaF}_2$  Powder (Fisher)  
2 = VHP #272  
3 = VHP #273

Results in ppm.

KEY:			
ND	- Not Detected	T	.01 - 1%
VVFT	< 0.001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

*J. R. Newberg*  
*L. R. Swift*  
 SUPERVISOR, TESTING LABS

can be seen, the teflon-treated material has the lowest cation impurity content, containing only alkaline earth impurities (Mg, Sr, and Ba) with no Na, Al, Cr, Mn, Fe, or Cu as is present in the as-received powder. The untreated casting is somewhat improved over the as-received powder but is not as impurity-free as teflon-treated material. The casting analyses compare (except for Mg, Sr, and Ba) with those of single crystal chips and castings made from such chips which have small amounts of Mg, Si, Cu and possibly Al and Fe for total analyzed cation impurity levels of 1.7 ppm and 1.1 ppm, respectively.<sup>1</sup> Table IV gives the limits of detection of impurities in  $\text{CaF}_2$  in these analyses.

In Tables V and VI are the results of the analyses on the following  $\text{SrF}_2$  samples: Table V - 1) As-received "reagent" grade powder, 2) Vacuum-baked powder, and 3) A casting (VHP-358, a remelt of VHP-357) initially using vacuum-baked powder and Table VI - 1) A casting (VHP-390) using 600°C teflon-treated and air-roasted powder, 2) A casting (VHP-393, a remelt) using 600°C teflon-treated and air-roasted powder, 3) A casting (VHP-394) using 600°C teflon-treated - no subsequent roast-powder, and 4) A casting (VHP-399) using teflon-treated material. Table VII gives the limits of detection of impurities in  $\text{SrF}_2$  in these analyses.

As can be seen in Tables V and VI, the as-received powder, vacuum-baked powder, and the casting from such are all rich in impurities as is the casting (VHP-390) from teflon-treated, air roasted powder. The casting (VHP-394) using teflon-treated-no roast-powder and the two remelts of powder (VHP-393 and 399) have mainly alkaline earth impurity (Ba, Ca, and Mg) contamination. Single crystal chips and a casting from such chips had similar alkaline earths as contaminants but at different levels of contamination.<sup>1</sup>

Clearly, these results show that castings of both  $\text{CaF}_2$  and  $\text{SrF}_2$  can be obtained with low cation impurity levels (with the exception of the alkaline earths) as was the case for ingots cast using single crystal chips.

As mentioned above, the early castings of  $\text{SrF}_2$  and  $\text{CaF}_2$  prepared from purified powder (and several castings prepared from single crystal chips) seemed quite susceptible to thermal shock cracking, being predominantly intergranular in nature. This behavior suggested weakened grain boundaries due to

TABLE IV

LIMITS OF DETECTION FOR ANALYSIS OF  $\text{CaF}_2$  SAMPLES



JARRELL-ASH DIVISION

Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co. DATE RECEIVED 10/17/74  
28 Seyon St. DATE REPORTED 11/27/74  
Waltham, MA 02154 ORDER NO.                     
ATTN: Mr. R. Newberg

SAMPLE DESCRIPTION Limits of Detection in  $\text{CaF}_2$  in ppm  
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

	x		x		x		x
U	25	1	Zn	10		Sb	5
Os	.1		Ge	1		Ta	40
B	1		Ge	1		Co	25
Na	10	.5	As	25		Be	5
Mg	.01		Rb	10	1	La	
Al	.1		Sr	5		Co	
Si	.1		V			Pr	
K	50	1	Zr	20		Nd	
Ca			Nb	40		Sm	
Tl	1		Mo	2		Eu	
V	5		Ru	10		Gd	
Cr	1		Rh	5		Tb	
Mn	.1		Pd	5		Dy	
Fe	1		Ag	.01		Ho	
Co	5		Cd	1		Er	
Ni	1		In	1		Tm	
Cu	.05		Sn	.5		Yb	
							Lu
							Hf
							Ta
							W
							Re
							Oe
							Ir
							Pt
							Au
							Hg
							Tl
							Ph
							Bi
							Th
							U
							P
							Se

REMARKS x = Separate analysis looking at high wavelength lines

KEY:		
ND	- Not Detected	T .01 - 1%
VVFT	< .0001%	L .1 - 1%
VFT	.0001% - .001%	M 1% - 10%
FT	.001% - .01%	H >10%

*C. Bonine*  
STAFF ANALYST

*C. Bonine*  
SUPERVISOR, TESTING LABS

TABLE V

ANALYSES OF "REAGENT" GRADE  $\text{SrF}_2$  SAMPLES



JARRELL-ASH DIVISION

Fisher Scientific Company

Certificate of Analysis

TO Raytheon Company DATE RECEIVED 2/4/75  
28 Seyon St. DATE REPORTED 2/6/75  
Waltham, MA 02154 ORDER NO 90-78360  
ATTN: Mr. R. Newberg, Mr. A. L. Sisson

SAMPLE DESCRIPTION  $\text{SrF}_2$   
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

	1	2	3		1	2	3		1	2	3		1	2	3
Li	ND	ND	ND	Zn	ND	ND	ND	Sb	ND	ND	ND	Lu			
Be	ND	ND	ND	Ga	ND	ND	ND	Te	ND	ND	ND	Hf	ND	ND	ND
B	ND	.5	.5	Ge	ND	ND	ND	Cs	ND	ND	ND	Ta	ND	ND	ND
Na	.1%	50	ND	As	ND	ND	ND	Ba	.3%	.3%	.3%	W	ND	ND	ND
Mg	.5	.5	.5	Rb	ND	ND	ND	La				Ra	ND	ND	ND
Al	.1	.5	.2	Sr	H	H	H	Ce				Os	ND	ND	ND
Si	ND	ND	.1	Y				Pr				Ir	ND	ND	ND
K	ND	ND	ND	Zr	ND	ND	ND	Nd				Pt	ND	ND	ND
Ca	ND	ND	ND	Nb	ND	ND	ND	Sn				Au	ND	ND	ND
Ti	ND	ND	ND	Mo	ND	ND	ND	Eu				Hg	ND	ND	ND
V	ND	ND	ND	Ru	ND	ND	ND	Gd				Tl	ND	ND	ND
Cr	2	2	1	Rh	ND	ND	ND	Tb				Pb	.5	1	20
Mn	.5	.1	.1	Pd	ND	ND	ND	Dy				Bi	ND	ND	ND
Fe	50	80	20	Ag	ND	ND	ND	Ho				Th			
Co	ND	ND	ND	Cd	ND	ND	ND	Er				U			
Ni	ND	ND	ND	In	ND	ND	ND	Tm				P	ND	ND	ND
Cu	20	10	ND	Sn	ND	ND	ND	Yb				Se			

REMARKS 1 = Reagent Lot #11839 as received  
2 = Reagent Lot #11839 vacuum baked  
3 = WHP-358  $\text{SrF}_2$  casting

Results in ppm.

KEY:			
ND	- Not Detected	T	.01 - 1%
VVFT	< .0001%	L	.1 - 1%
VFT	.0001% - .001%	M	1% - 10%
FT	.001% - .01%	H	>10%

STAFF ANALYST

SUPERVISOR, TESTING LABS

*C. Bonomi*

TABLE VI

ANALYSES OF "REAGENT" GRADE  $\text{SrF}_2$  SAMPLES

JARRELL-ASH DIVISION

Fisher Scientific Company

## Certificate of Analysis

TO: Raytheon Co. DATE RECEIVED 4/4/75  
28 Saxon St. DATE REPORTED 4/11/75  
Waltham, MA 02154 ORDER NO. 90-78807  
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

SAMPLE DESCRIPTION  $\text{SrF}_2$   
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

	1	2		1	2		1	2		1	2
U	ND	ND	Zn	ND	ND		Sb	ND	ND	Lu	
Be	ND	ND	Ge	ND	ND		Ta	ND	ND	Hf	ND
B	ND	ND	Ge	ND	ND		Cs	ND	ND	Ta	ND
Na	ND	ND	As	ND	ND		Ba	1%	.05%	W	ND
Mg	1	.5	Rb	ND	ND		La			Re	ND
Al	.1	ND	Sr	H	H		Ce			Os	ND
Si	.1	ND	Y				Pr			Ir	ND
K	ND	ND	Zr	ND	ND		Nd			Pt	ND
Ca	100	100	Nb	ND	ND		Sn			Au	ND
Ti	ND	ND	Mo	ND	ND		Eu			Hg	ND
V	ND	ND	Ru	ND	ND		Gd			Tl	ND
Cr	3	ND	Rh	ND	ND		Tb			Pb	ND
Mn	.01	ND	Pd	ND	ND		Dy			Bi	ND
Fe	.1	ND	Ag	ND	ND		Ho			Th	
Co	ND	ND	Cd	ND	ND		Er			U	
Ni	ND	ND	In	ND	ND		Tm			P	ND
Cu	.01	.05	Sn	ND	ND		Yb			Se	ND

REMARKS 1 = VHP 390  
2 = VHP 393  
Results in ppm.

KEY:	
ND	- Not Detected
VVFT	< .0001%
VFT	.0001% - .001%
FT	.001% - .01%
T	.01 - 1%
L	.1 - 1%
M	1% - 10%
H	> 10%

P. Resnick

STAFF ANALYST

L. Resnick

SUPERVISOR, TESTING LABS

TABLE VI (Cont'd.)

ANALYSES OF "REAGENT" GRADE SrF<sub>2</sub> SAMPLES



JARRELL-ASH DIVISION

Fisher Scientific Company

**Certificate of Analysis**

TO: Raytheon Co.  
28 Seyon St.  
Waltham, MA 02154  
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

SAMPLE DESCRIPTION: SrF<sub>2</sub>  
INSTRUMENTATION: 3.4 Meter Ebert Mark IV Spectrograph

DATE RECEIVED: 4/4/75  
DATE REPORTED: 4/11/75  
ORDER NO: 90-78807

	3	4		3	4		3	4		3	4	
U	ND	ND	Zn	ND	ND		Sb	ND	ND	Lu		
Be		ND	Ge	ND	ND		Te	ND	ND	Hf	ND	ND
B	ND	ND	Ge	ND	ND		Cs	ND	ND	Ta	ND	ND
Na	ND	ND	As	ND	ND		Be	.5%	.3%	W	ND	ND
Mg	.1	.1	Rb	ND	ND		La			Re	ND	ND
Al	ND	ND	Sr	H	H		Ce			Os	ND	ND
Si	ND	ND	Y				Pr			Ir	ND	ND
K	ND	ND	Zr	ND	ND		Nd			Pr	ND	ND
Ca	70	70	Nb	ND	ND		Sn			Au	ND	ND
Ti	ND	ND	Mo	ND	ND		Eu			Hg	ND	ND
V	ND	ND	Ru	ND	ND		Gd			Tl	ND	ND
Cr	ND	ND	Rh	ND	ND		Tb			Pb	ND	ND
Mn	ND	ND	Pd	ND	ND		Dy			Bi	ND	ND
Fe	ND	ND	Ag	.01	ND		Ho			Th		
Co	ND	ND	Cd	ND	ND		Er			U		
Ni	ND	ND	In	ND	ND		Tm			P	ND	ND
Cu	ND	.01	Sn	ND	ND		Yb			Se		

REMARKS: 3 = VHP 394  
4 = VHP 399  
Results in ppm

*L. Brown*  
STAFF ANALYST

*L. Brown*  
SUPERVISOR, TESTING LABS

KEY:  
ND - Not Detected    T .01 - .1%  
VVFT < .0001%    L 1- 1%  
VFT .0001% - .001%    M 1% - 10%  
FT .001% - .01%    H >10%

TABLE VII

LIMITS OF DETECTION FOR ANALYSIS OF  $\text{SrF}_2$  SAMPLES



JARRELL-ASH DIVISION

Fisher Scientific Company

Certificate of Analysis

TO: Raytheon Co. DATE RECEIVED 4/4/75  
28 Seyon St. DATE REPORTED 4/11/75  
Waltham, MA 02154 ORDER NO. 90-78807  
ATTN: Mr. R. Newberg - Mr. A. L. Sisson

SAMPLE DESCRIPTION Limits of detection in  $\text{SrF}_2$  in ppm  
INSTRUMENTATION 3.4 Meter Ebert Mark IV Spectrograph

U	25	Zn	10	Sb	5	Lu	
Be	.1	Ge	1	Te	40	Mt	50
B	1	Ge	1	Cs	25	Ta	50
Na	10	As	25	Be	1	W	50
Mg	.01	Rb	10	La		Ro	20
Al	.1	Sr	-	Co		Os	20
Si	.1	Y		Pr		Ir	20
K	50	Zr	20	Nd		Pr	5
Ca	.1	Nb	40	Sn		Au	2
Ti	2	Mo	1	Eu		Mg	50
V	5	Ru	10	Gd		Tl	50
Cr	.1	Rh	5	Tb		Po	.5
Mn	.05	Pd	5	Dy		Bi	.5
Fe	1	Ag	.01	Ho		Tm	
Co	1	Cd	1	Er		U	
Ni	1	In	.5	Tm		P	25
Cu	.01	Sn	.5	Ta		Se	

REMARKS: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

*C. Bonini*  
STAFF ANALYST

*C. Bonini*  
SUPERVISOR, TESTING LABS

KEY:	
ND	- Not Detected
VVFT	< .0001%
VFT	.0001% - .001%
FT	.001% - .01%
	H >10%

impurity precipitation and led to further investigation which solved the problem as mentioned above. Samples of three cast fluorides -  $\text{BaF}_2$ ,  $\text{SrF}_2$ , and  $\text{CaF}_2$  (VHP-147, 311, and 317, respectively) that failed intergranularly were investigated by X-ray microprobe analysis and SEM (scanning electron microscopy). Microprobe analysis of impurities and their distribution in these samples indicated a weak, uniformly distributed contamination of Al (in  $\text{CaF}_2$  and  $\text{BaF}_2$ ), Ca (in  $\text{SrF}_2$ ), and Sr (in  $\text{BaF}_2$ ). In addition, the grain boundary surfaces showed localized accumulations containing predominantly Na, S, Cl, K and occasionally also Mg, Si, Fe, and Zn. These accumulations seemed to be located in surface irregularities such as holes, cracks, and precipitates. To obtain a clearer correlation between surface appearance and impurity content, magnified maps of the grain boundary surfaces were produced from overlapping SEM pictures. Specific irregularities were identified and subjected to microprobe analysis, the results of which follow.

Figures 3 and 4 illustrate the example of  $\text{BaF}_2$  (VHP-147). Figure 3a shows the general surface area with irregularity at the intersection of two grains. The precipitate is shown at higher magnification in Fig. 3b. Care was taken to avoid contamination of the surfaces during handling, but it is not entirely clear in this case if the precipitate is not a result of handling. Figure 4a is the overall X-ray spectra from microprobe analysis of both the general uniform distribution of the grain boundary surface (designated matrix) and the precipitate (designated location 1). Figure 4b is the stripped X-ray spectrum of the precipitate; i.e., the matrix spectrum is subtracted from the precipitate spectrum. Any differences in impurity concentrations between the two are shown as sharp peaks in the stripped spectrum. In this case the precipitate is enriched in K, S, and Cl.

Similarly, Figs. 5a and 5b show the grain boundary fracture surface of  $\text{SrF}_2$  (VHP-311) with several irregularities and a magnification of a similar irregularity, respectively. Such irregularities appear to be precipitates torn from the matrix during fracture and are clearly not contaminants from handling. Figures 6a and 6b show the X-ray spectra for the two areas - the matrix (no precipitates probed) and precipitate (designated location 1, the latter showing the area to be enriched in Na, K, and Cl).

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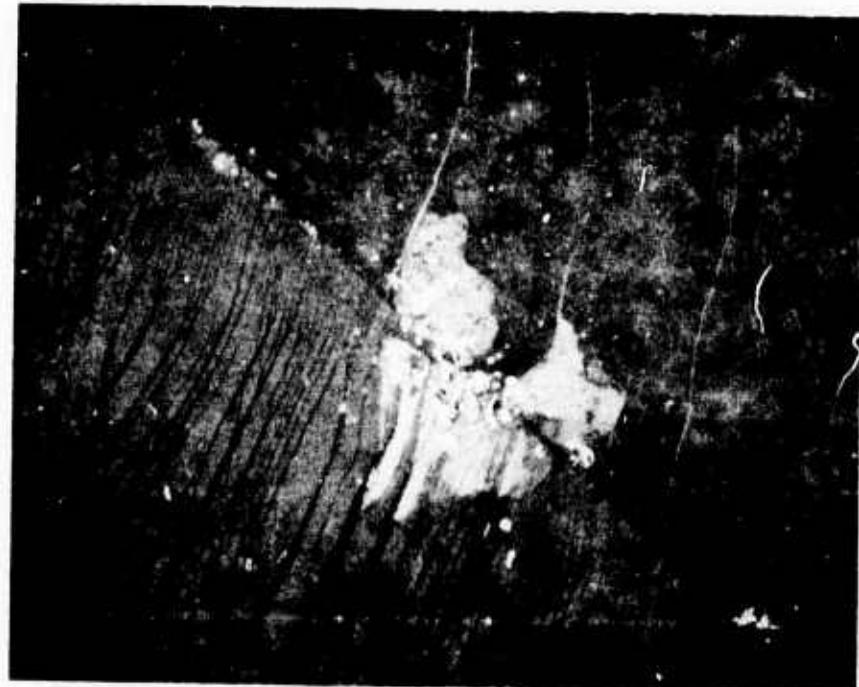


Fig. 3a Fracture Surface of Cast BaF<sub>2</sub> Sample. SEM 200 $\times$

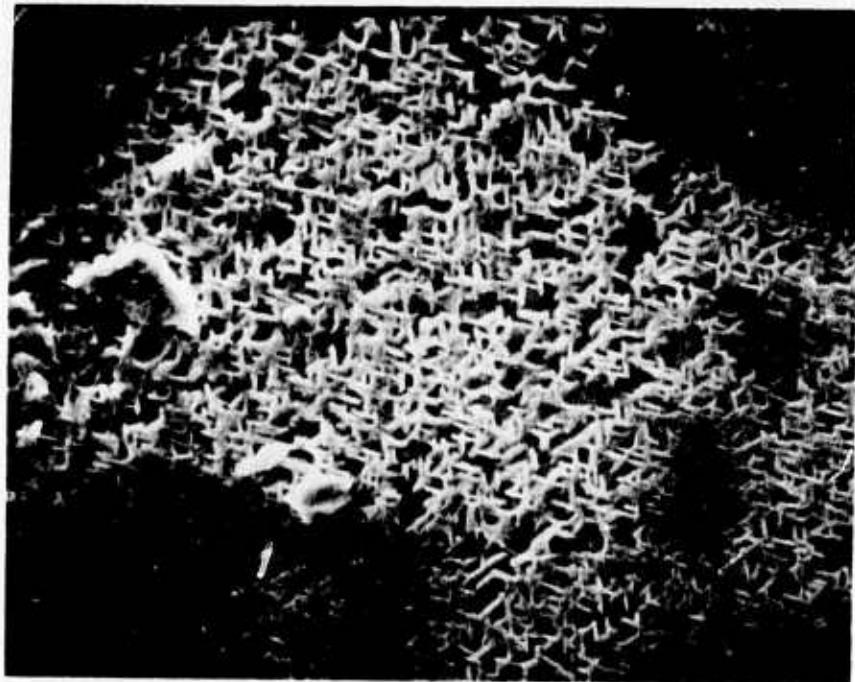
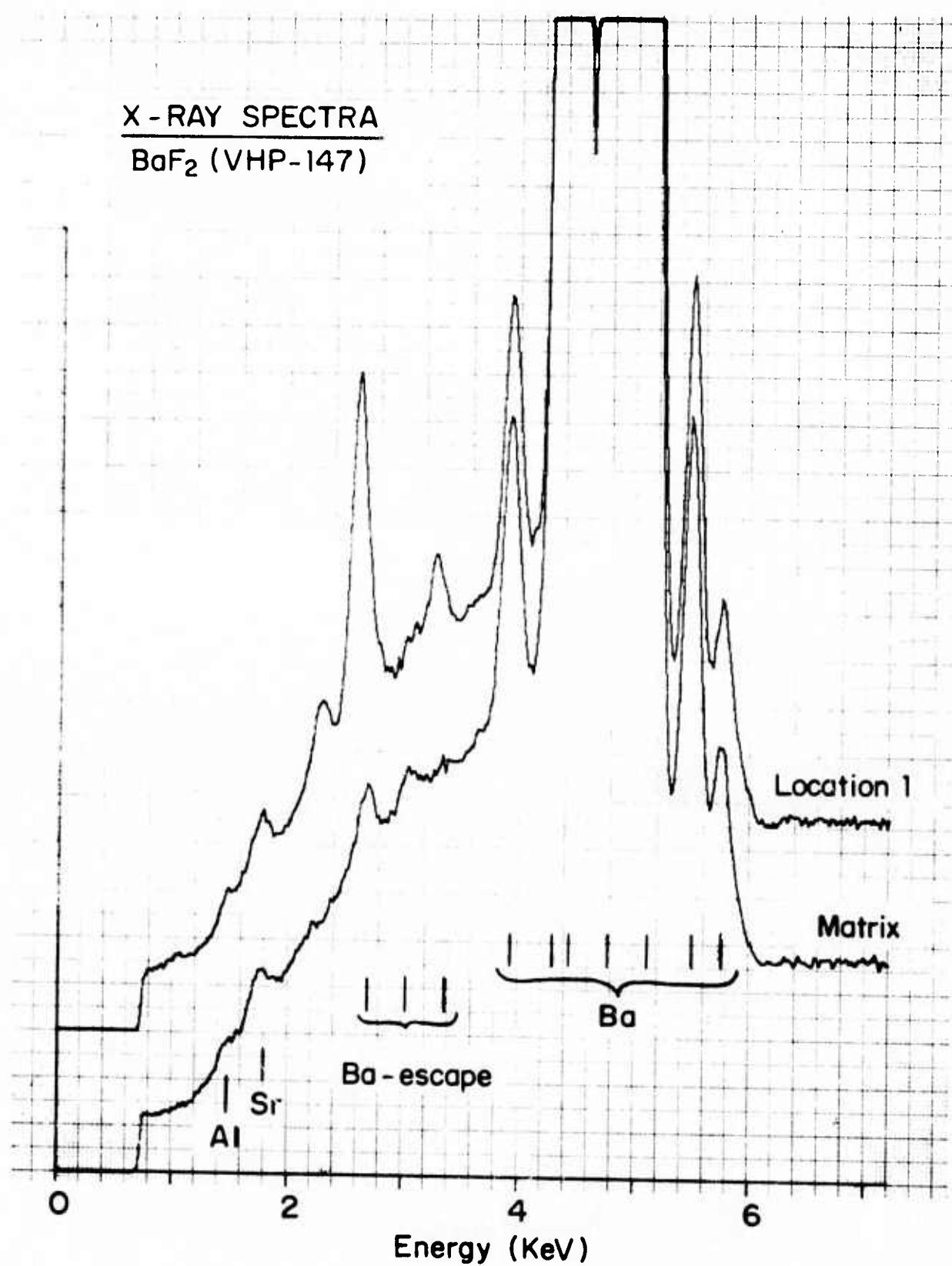
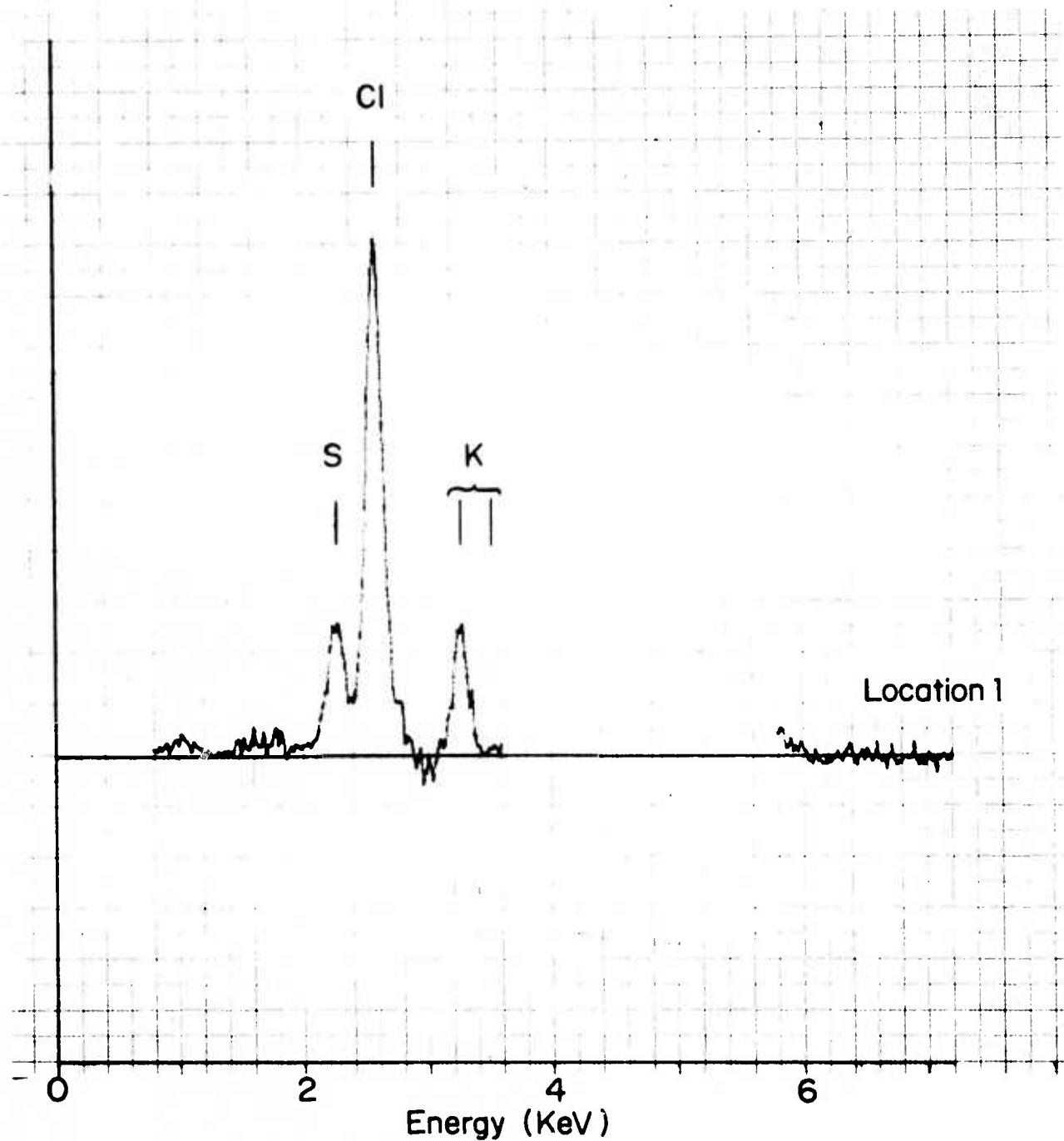


Fig. 3b Precipitate Area at Fracture Surface of Cast BaF<sub>2</sub> Sample. SEM 2000 $\times$

Fig. 4a X-Ray Spectra of Cast  $\text{BaF}_2$  Sample

STRIPPED X-RAY SPECTRUM  
 $\text{BaF}_2$  (VHP-147)



4b Stripped X-Ray Spectrum of Cast  $\text{BaF}_2$  Sample

PBN-75-80

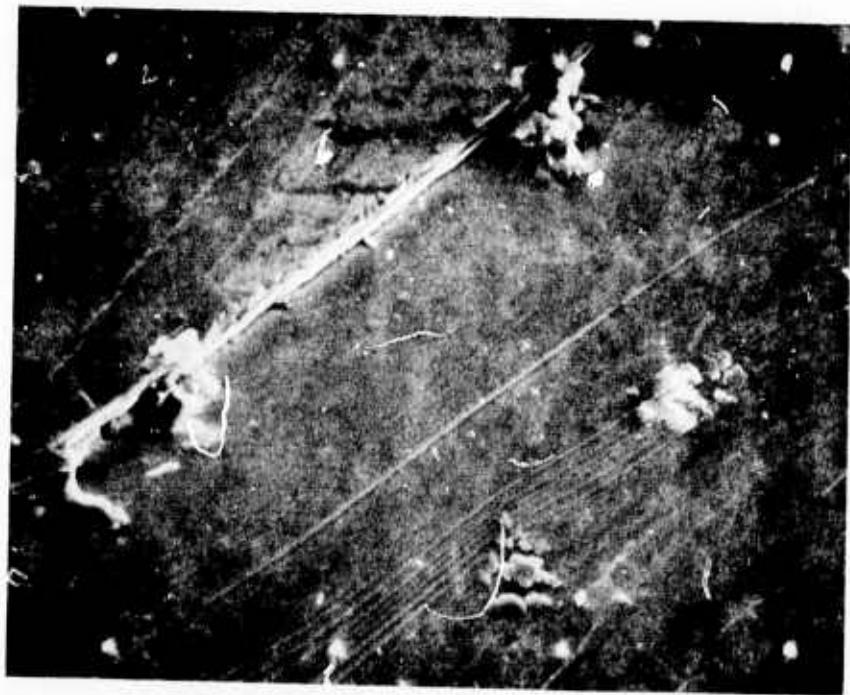


Fig. 5a Fracture Surface of Cast SrF<sub>2</sub> Sample. SEM 700 $\times$



Fig 5b Fracture Surface of Cast SrF<sub>2</sub> Sample. SEM 2000 $\times$

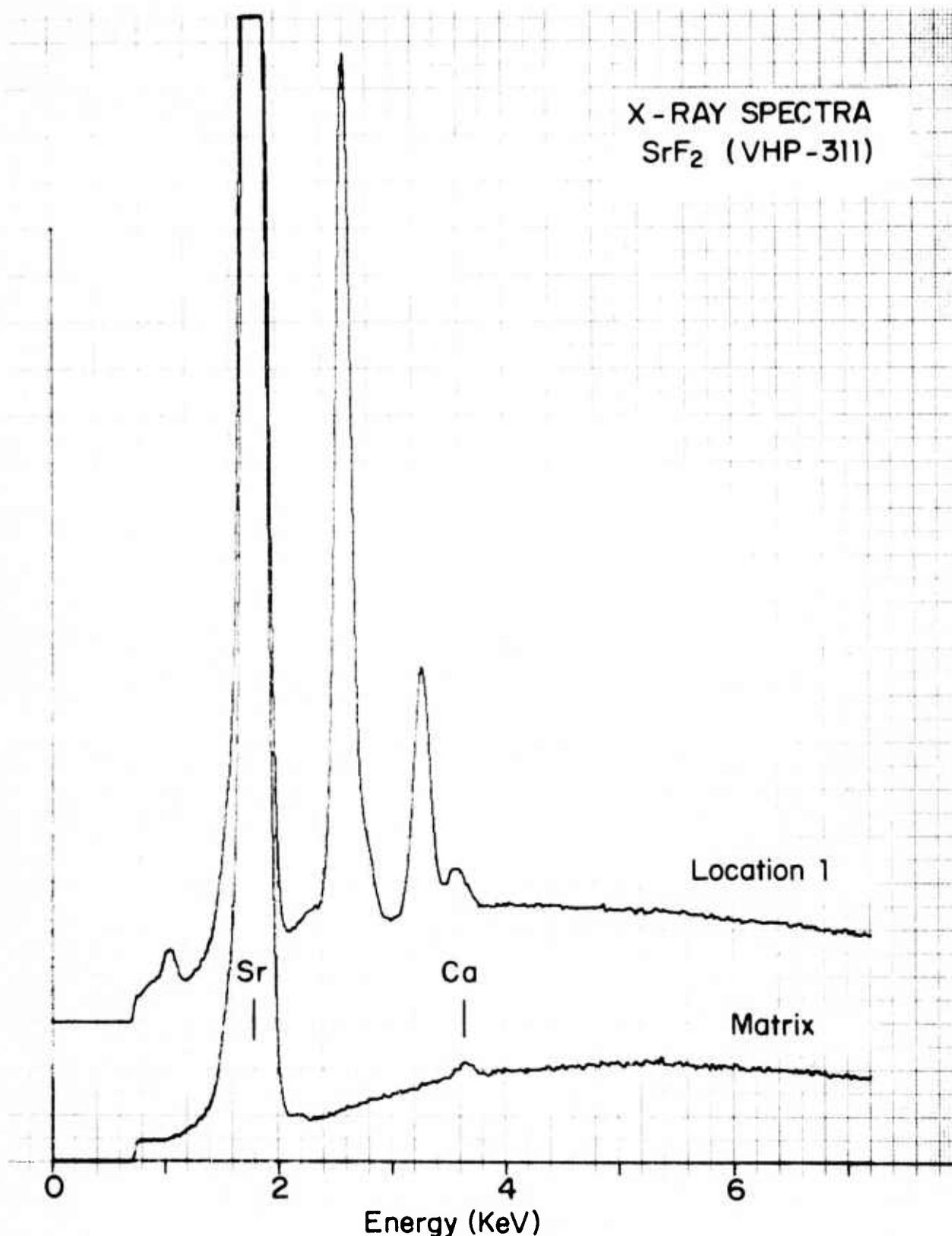


Fig. 6a X-Ray Spectra of Cast  $\text{SrF}_2$  Sample

STRIPPED X-RAY SPECTRUM  
 $\text{SrF}_2$  (VHP-311)

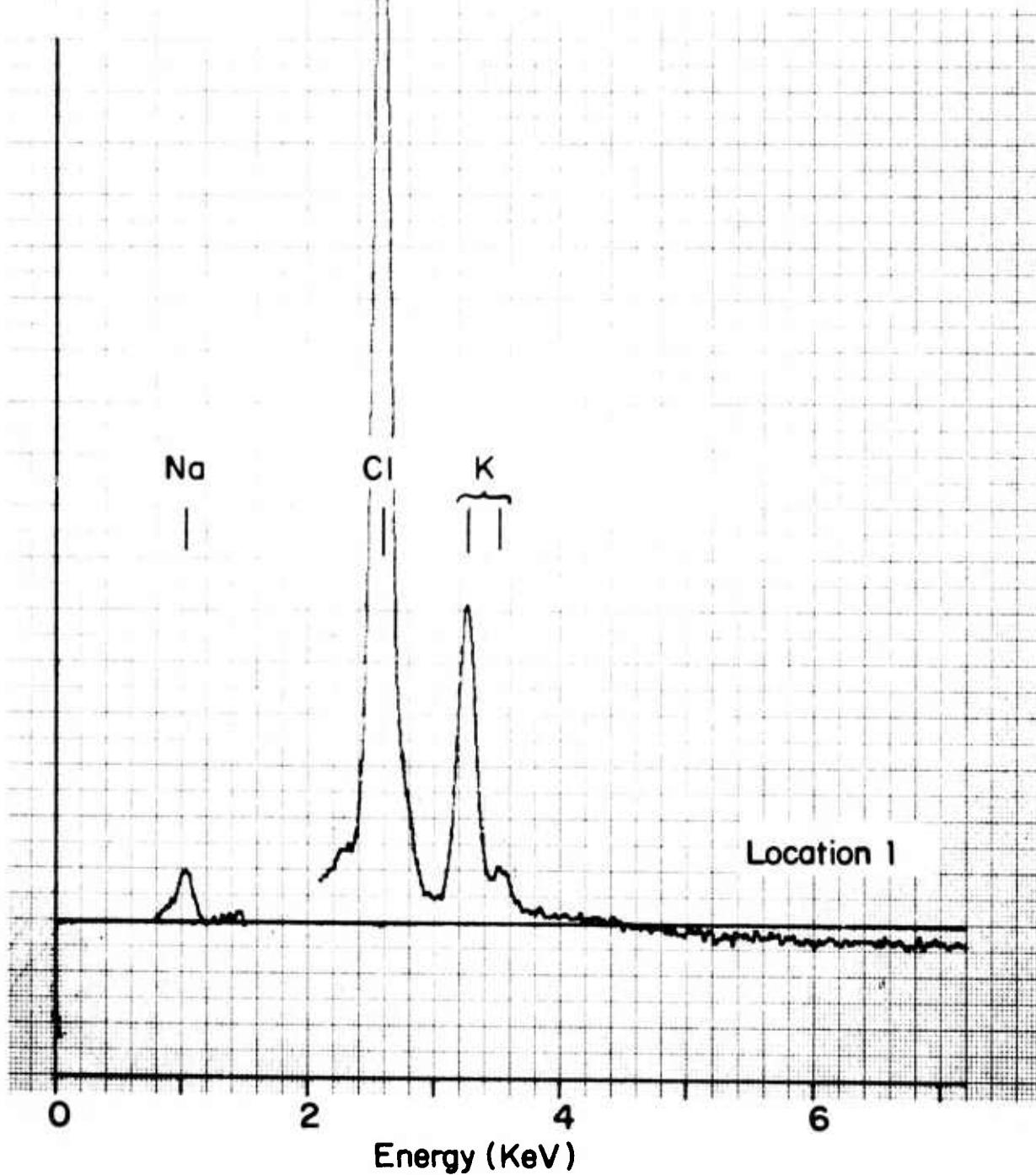


Fig. 6b Stripped X-Ray Spectrum of Cast  $\text{SrF}_2$  Sample

Finally, Figs. 7a - e show similar grain boundary surfaces of cast  $\text{CaF}_2$  (VHP-317) and three quite different surface irregularities (designated locations 1, 2, and 3 in the X-ray spectra of Figs. 8a and 8b). It can also be noted (Figs. 7a and 7b) by the rippled effect of the general surface that true intergranular failure occurred, whereas for the  $\text{BaF}_2$  and  $\text{SrF}_2$ , cleavage steps are also present. From the X-ray spectra of Fig. 8a it can be seen that the  $\text{CaF}_2$  matrix has few impurities. However, the irregularities are quite rich and substantially different from each other, as best seen in the stripped X-ray spectra of Fig. 8b. The protruding mass of location 1 is enriched mainly in Mg, Al, Si, and Fe; while what appears to be a hole at location 2 is enriched in Si, S, Cl, and K. Finally, the white precipitate at location 3 is enriched mainly in Na, Si, Cl, and K.

The above results indicate that the bulk of the contamination may be localized in accumulations at the grain boundaries. Whether or not these impurities seriously affect the mechanical properties (such as thermal shock resistance) is not quantitatively known. Further effort is being planned to fully evaluate their effect.

## 2.2 Inert Atmosphere Casting

During this period, work was initiated to develop a casting technique in an inert atmosphere instead of the high vacuum ( $10^{-4}$  torr or better) required normally. The advantage of inert atmosphere operation is that unidirectional solidification may be better accomplished due to the better heat transfer provided by the gas. It is also desirable because, in the event of scale-up to larger sizes, an inert atmosphere may be less expensive and more convenient to provide than a high vacuum system.

A series of castings of  $\text{CaF}_2$  were attempted in the vacuum hot press furnace using dry, high purity argon (passed over titanium chips at 800 - 900°C to remove residual  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) to provide partial pressures of 1, 5, 15, 25, and 50 torr. The castings are listed in Table 1. As expected, better heat transfer resulted in complete unidirectional solidification in all but two of the castings (VHP-301 and 317). However, except for these same two castings, as well as VHP-375, the inert atmosphere castings were all

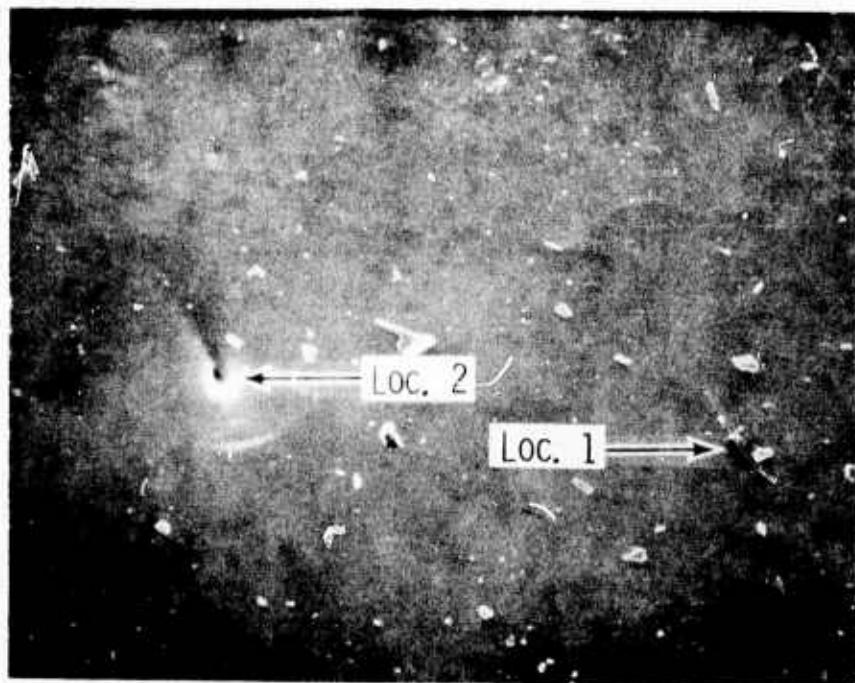


Fig. 7a Fracture Surface of Cast  $\text{CaF}_2$  Sample. SEM 100 $\times$

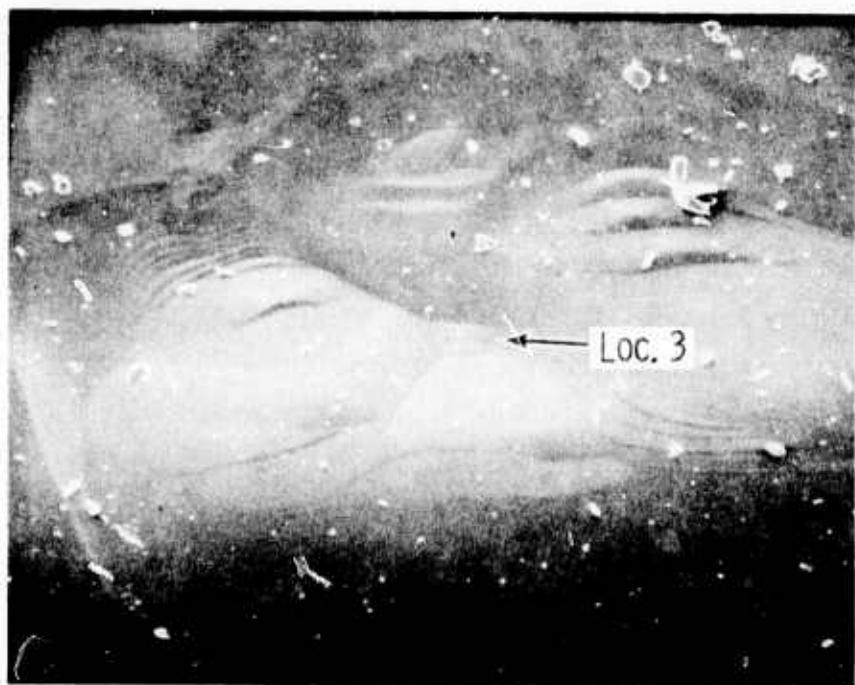


Fig. 7b Fracture Surface of Cast  $\text{CaF}_2$  Sample. SEM 100 $\times$

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PBN-75-84

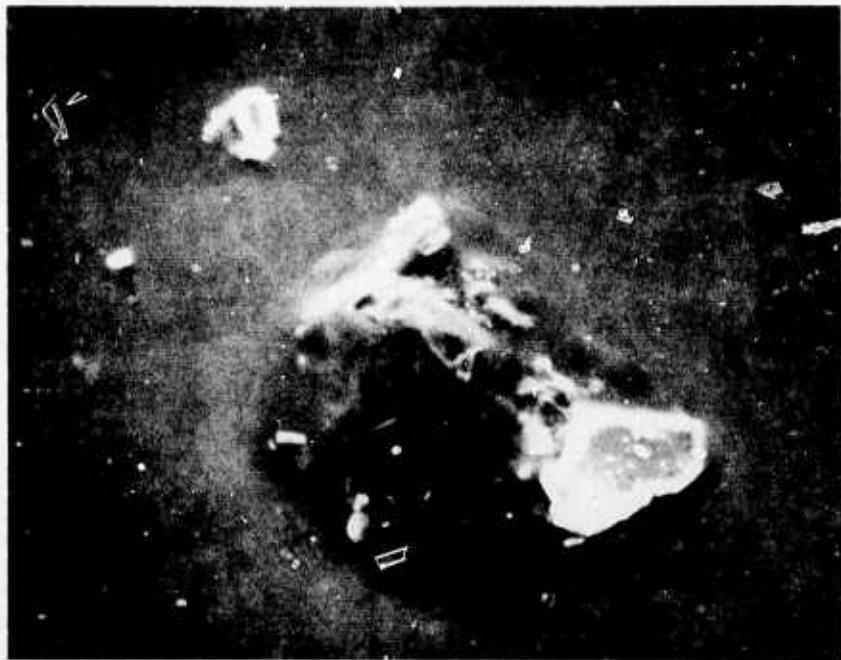


Fig. 7c Location 1. SEM 1000 $\times$



Fig. 7d Location 2. SEM 1000 $\times$

PBN-75-85



Fig. 7e Location 3. SEM 3000 X

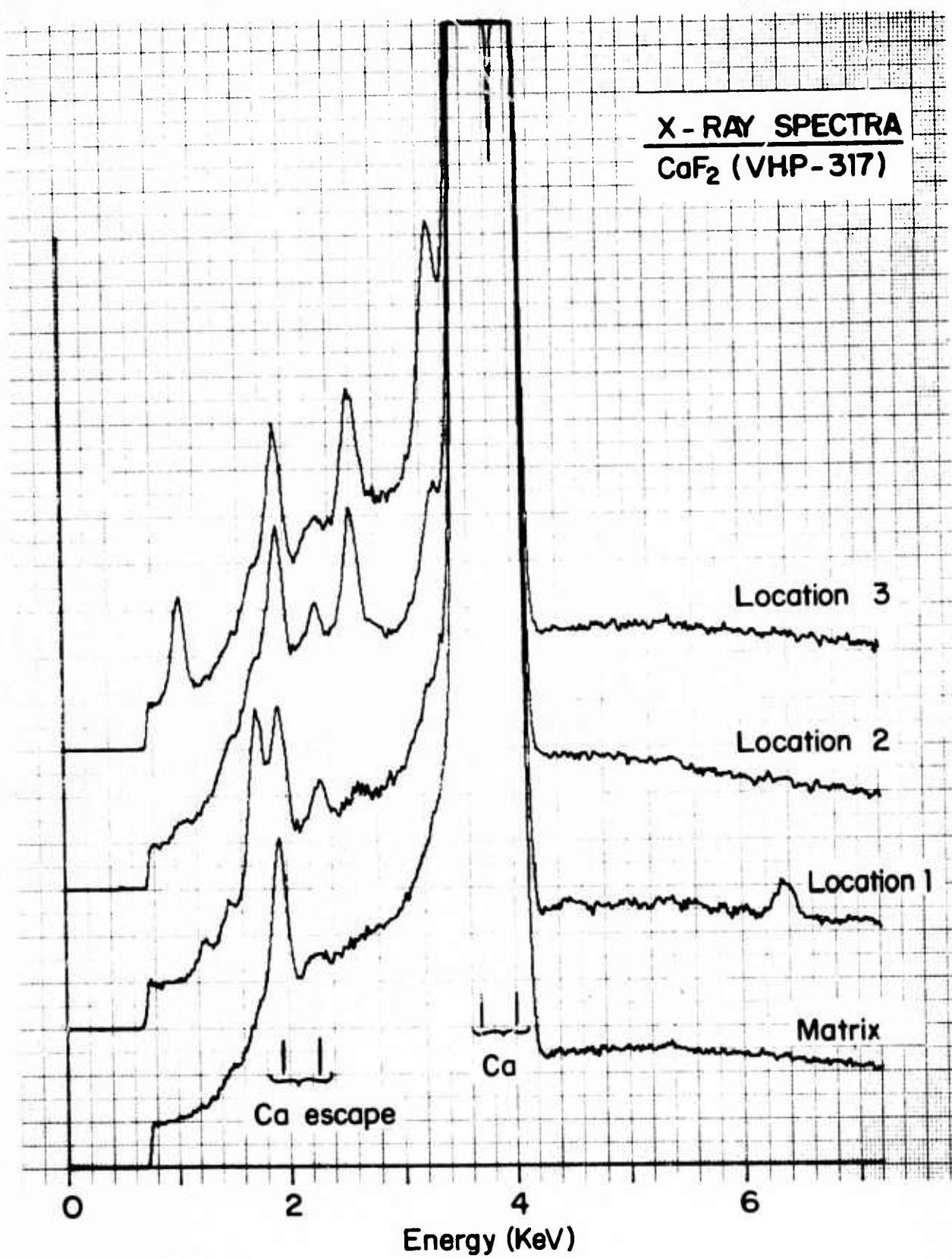
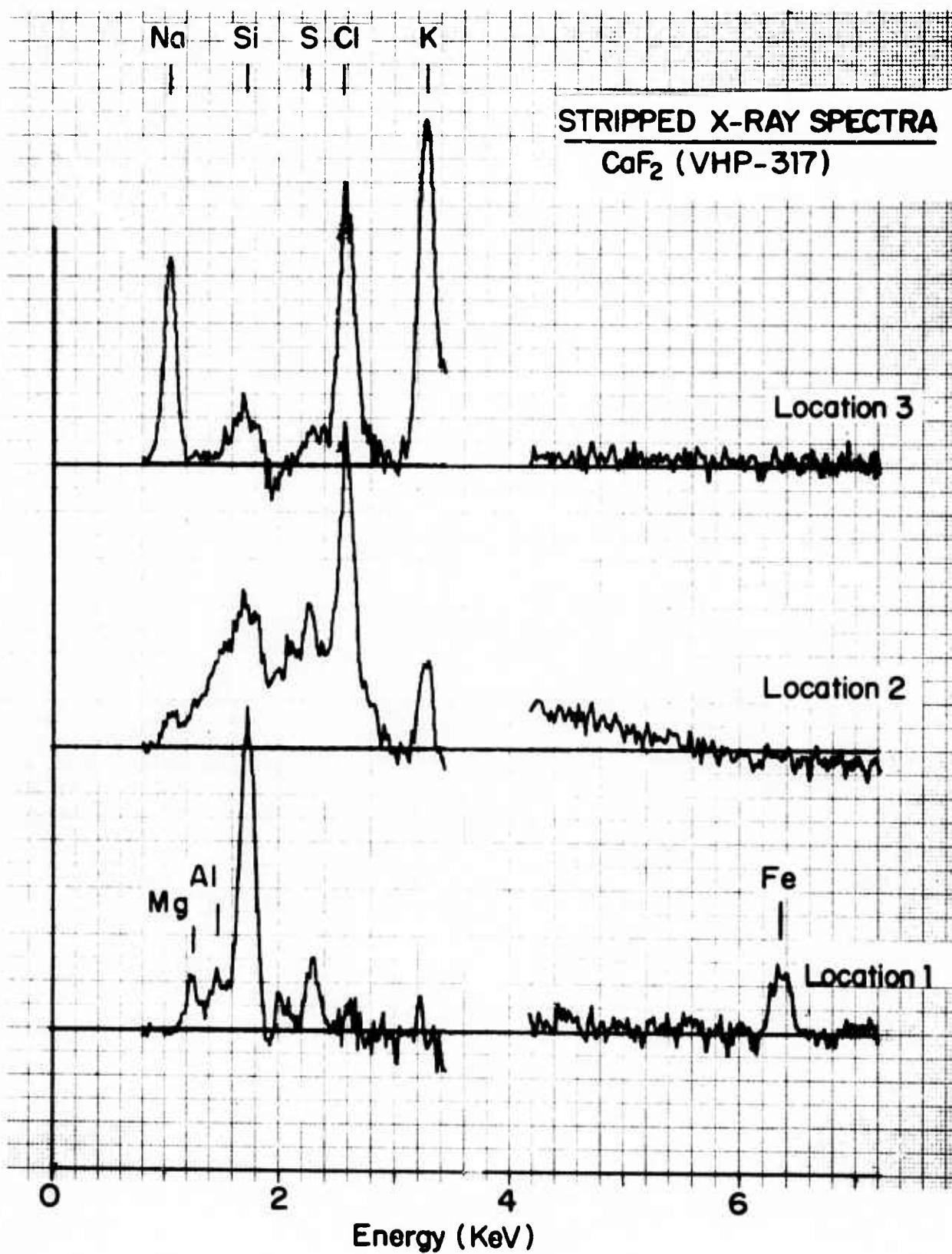


Fig. 8a X-Ray Spectra of Cast  $\text{CaF}_2$  Sample

Fig. 8b Stripped X-Ray Spectra of Cast  $\text{CaF}_2$  Sample

slightly discolored (a yellowish to bluish tinge) indicating that the atmosphere was not sufficiently inert and that there was impurity pickup in the castings. Further attempts are presently under way to improve the technique.

### 2.3 Hot Forging

During this reporting period only two hot forgings were attempted, as listed in Table I. One-inch diameter samples were core drilled from a polycrystalline casting of  $\text{CaF}_2$  (VHP-302 and 303) in the vacuum hot press furnace. Both were successfully forged, but, as was the case with hot forged single crystal samples of  $\text{CaF}_2$ ,<sup>1</sup> the resultant grain size was large (on the order of several millimeters) due to the high forging temperature. No further work on hot forging is presently being planned because of the very good mechanical properties of the castings as will be discussed later.

### 2.4 Strain Annealing

One of the major problems with the fusion casting of the fluorides is the residual strain present in the ingots cast in the vacuum hot press furnace, due to rapid or uneven cooling. The problem was alleviated somewhat, as mentioned earlier, by the furnace modification allowing controlled cooling to room temperature from the solidification temperatures. However, the cast ingots still come out strained (Fig. 9) and must be strain-annealed prior to subsequent handling. The strain annealing procedure that has been used extensively during this period is the same as that developed during the first six months, i.e., annealing at  $900^\circ\text{C}$  for 10 hours followed by controlled cooling at  $25^\circ\text{C}/\text{hr}$ . to room temperature. Samples of cast  $\text{SrF}_2$  thus annealed show marked strain reduction, but as Fig. 10 illustrates, the procedure is not entirely successful in producing completely strain-free material. However, with the strain reduction achieved, further handling of the cast ingots could be done, e.g., core drilling, cutting, grinding, and polishing, without marked susceptibility to cracking. However, with the installation of the high vacuum system for the two-zone annealing furnace, several attempts were made late in this period to anneal  $\text{SrF}_2$  at a higher temperature, i.e., at

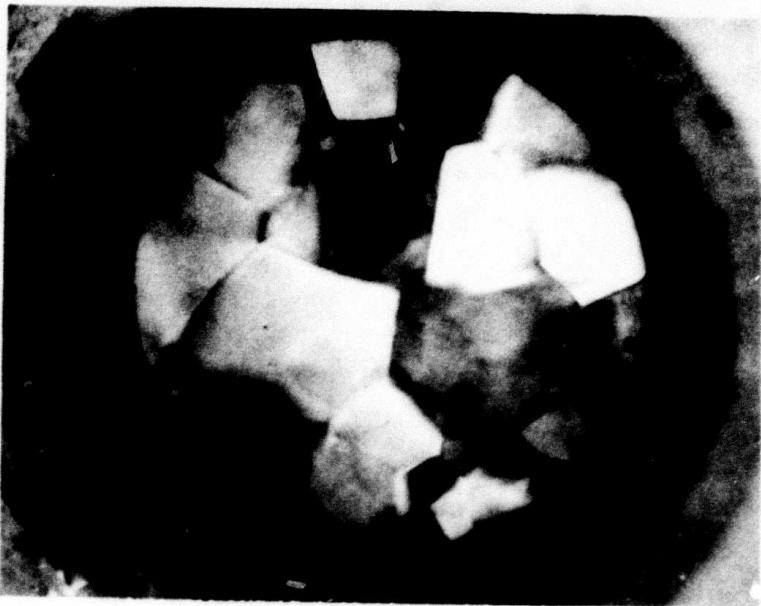


Fig. 9 Cast  $\text{SrF}_2$ , as Cast. Viewed through crossed polarizers.

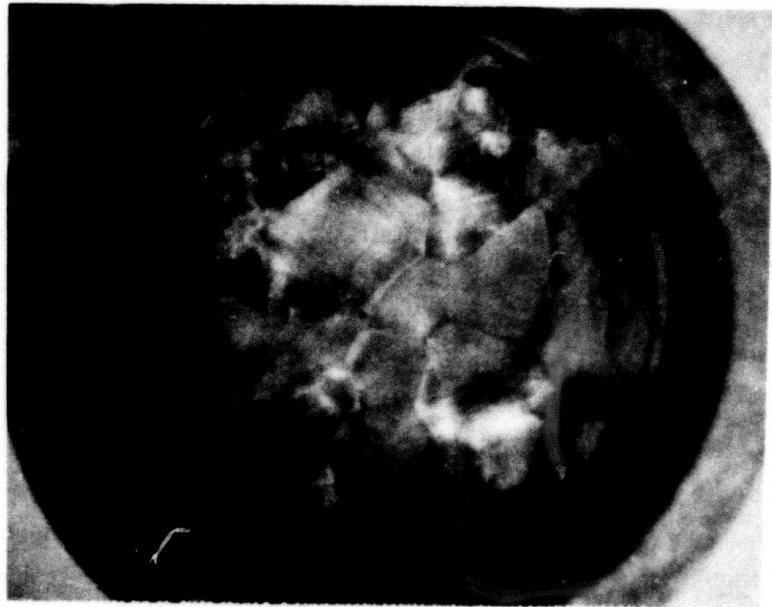


Fig. 10 Cast  $\text{SrF}_2$  (VHP-343) After 900°C Anneal for 10 hrs. and Cooled at 25°C/hr. Viewed through crossed polarizers.

1000°C under high vacuum ( $10^{-4}$  -  $10^{-5}$  torr). The initial results are successful as Fig. 11 illustrates. The ingot is fairly strain-free after annealing at 1000°C for 10 hours followed by controlled cooling at 25°C/hr. to room temperature.

During the third quarter, a large Lindberg box furnace was installed in the laboratory. It has heating and cooling capabilities at controlled rates of about 10 - 100°C/hr. (subject to the natural heating and cooling rates of the furnace) from room temperature to 1500°C.

By using an Inconel inert atmosphere retort (approximately 10 x 10 x 12 inches inner dimensions) preliminary strain anneal runs in an inert atmosphere were attempted in this furnace. Samples were one-inch diameter single crystals of  $\text{CaF}_2$  (Optovac). The procedure for each heat treatment was to heat the furnace at 50°C/hr. to the soak temperature after purging the system as desired. The soak temperature (800, 900, or 1000°C) was held for ten hours, followed by cooling at 25°C/hr. to room temperature. Table VIII presents the results of these runs. The samples heated in air or argon at 1000°C showed fine white precipitates distributed either uniformly throughout (opacity) or as veils. Samples heated in argon or helium without sufficient purging at 900°C also showed some opacity. However, samples annealed at 800 or 900°C and properly purged with argon were as transparent as before and showed no scattering (as viewed with a He-Ne laser beam). So for  $\text{CaF}_2$ , annealing at 900°C in argon may be a viable alternative to vacuum annealing at 900°C.

However, since vacuum annealing of  $\text{SrF}_2$  was more successful at 1000°C and since the above results for  $\text{CaF}_2$  indicate a maximum useful annealing capability in argon of only 900°C without impurity pickup, an alternative was tried. That is, the  $\text{SrF}_2$  sample to be annealed is placed in a closed crucible with pieces of teflon and subsequently annealed at 1000°C, the teflon vapors providing a "purifying" atmosphere. The results of several runs were mixed but encouraging. That is, there is strain reduction but the procedure must be developed further before a final analysis is given.

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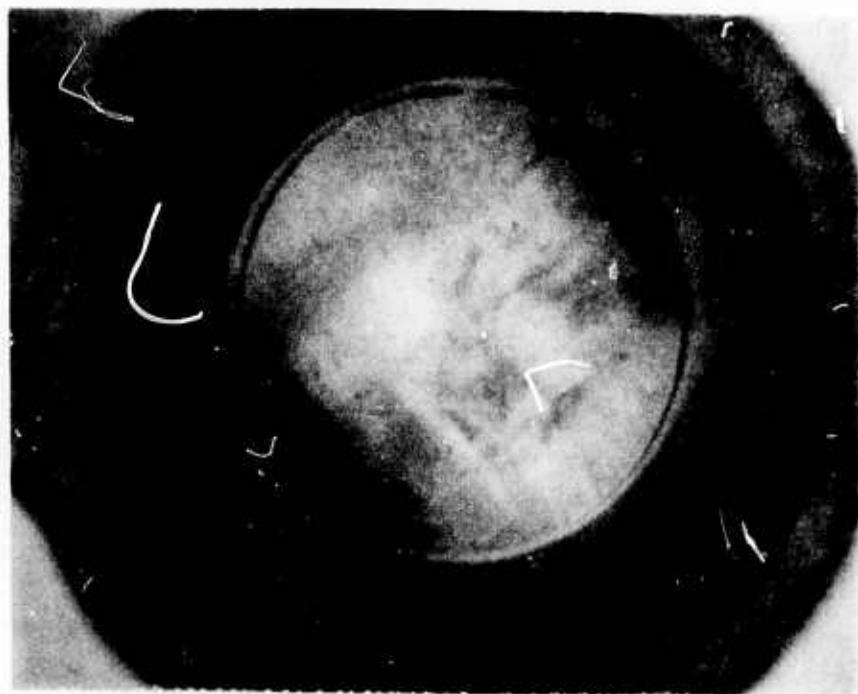


Fig. 11 Cast  $\text{SrF}_2$  (VHP-395) After  $1000^\circ\text{C}$  Anneal for 10 hrs. and Cooled at  $25^\circ\text{C}/\text{hr}$ . Viewed through crossed polarizers.

TABLE VIII  
EFFECT OF HEAT TREATMENT ON  $\text{CaF}_2$  SINGLE CRYSTALS

<u>Heat Treatment Temperature (°C)</u>	<u>Atmosphere</u>	<u>Comments</u>
1000	Air	Sample opaque
900	Argon (unpurged)	Sample uniformly hazy
900	Helium (unpurged)	Sample uniformly hazy
1000	Argon (purged 24 hrs.)	Veils throughout
900	Argon (purged 24 hrs.)	No haziness or scatter
800	Argon (purged 24 hrs.)	No haziness or scatter

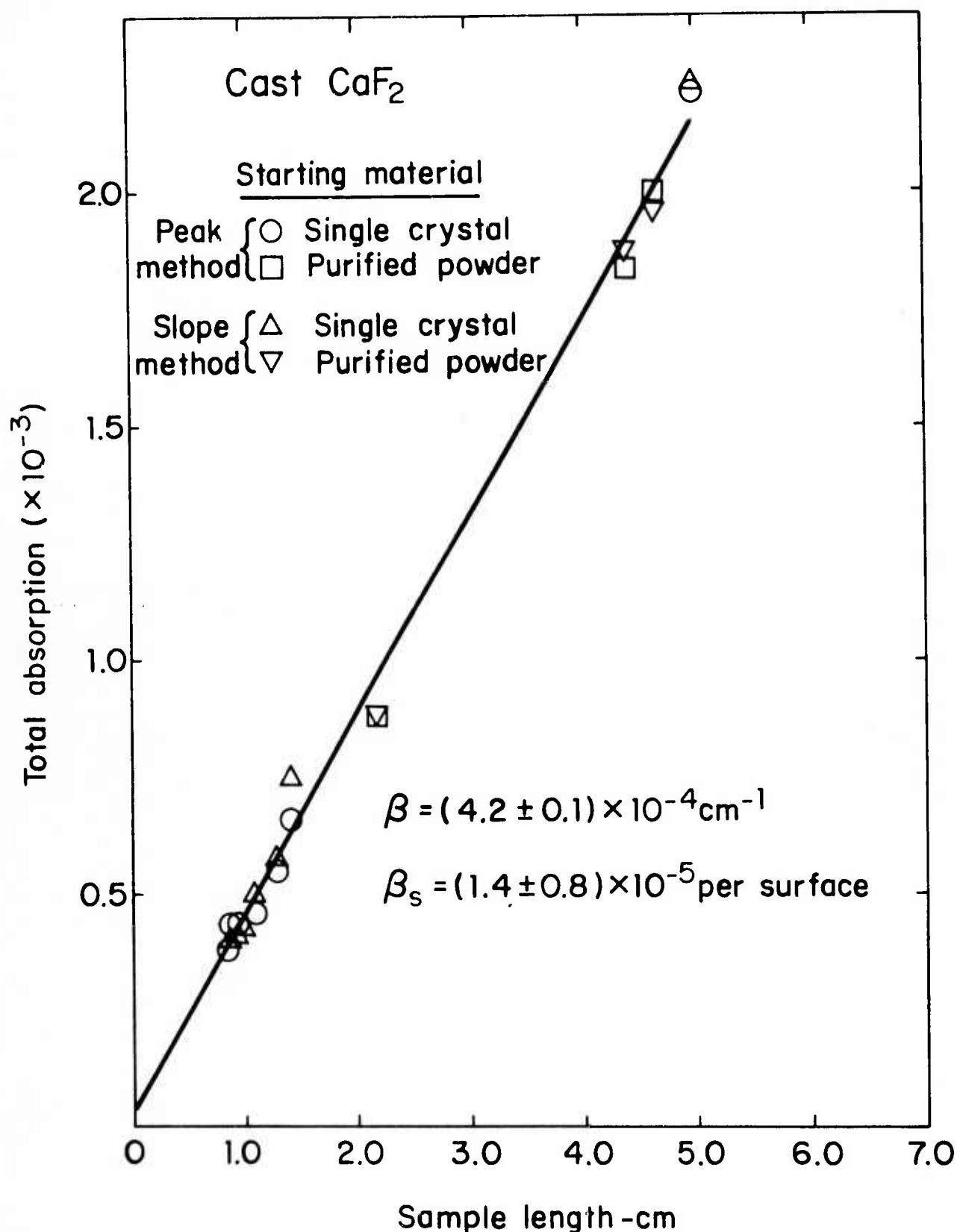
## 2.5 Optical Properties

The feasibility of casting consistently high quality  $\text{SrF}_2$  and  $\text{CaF}_2$  has been demonstrated by using either high purity single crystal chips or purified "reagent" grade powder as starting materials. Loss measurements done by laser calorimetry were made at  $5.25\mu\text{m}$  for  $\text{CaF}_2$  (both purified powder and single crystal starting material),  $\text{SrF}_2$  (single crystal starting material), and  $\text{SrF}_2$  (purified powder starting material). Figures 12, 13, and 14, respectively, plot the total absorption versus length for these castings. Note that the measurements for cast  $\text{CaF}_2$  fall on the same line regardless of the starting material (Fig. 12).

The results are summarized in Table IX for both  $\text{CaF}_2$  and  $\text{SrF}_2$ . The average  $5.25\mu\text{m}$  bulk\* absorption coefficient of cast  $\text{CaF}_2$  ingots is  $(4.2 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$  - 14 measurements on 10 ingots - results essentially equivalent to the measured value for single crystal  $\text{CaF}_2$  and quite near the value of  $1.8 \times 10^{-4} \text{ cm}^{-1}$  predicted<sup>2</sup> from the exponential law. The results for an ingot of  $\text{SrF}_2$  cast from single crystal chips show an average  $5.25\mu\text{m}$  bulk absorption coefficient -  $(6.7 \pm 1.0) \times 10^{-5} \text{ cm}^{-1}$  - near the value -  $(4.1 \pm 0.7) \times 10^{-5} \text{ cm}^{-1}$  - for single crystal  $\text{SrF}_2$  as reported by Deutsch<sup>2</sup> and near the value of  $2 \times 10^{-5} \text{ cm}^{-1}$  predicted<sup>2</sup> from the exponential law. The present results show a higher value -  $(1.7 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$  - for one ingot of  $\text{SrF}_2$  cast from purified powder. However, further work is underway with purified-powder castings since the results for  $\text{CaF}_2$  are so encouraging.

The above results show clearly that for both  $\text{CaF}_2$  and  $\text{SrF}_2$ , the fusion casting process does not degrade the optical properties of high purity single crystal starting material. Furthermore, it has been shown that an all graphite system is capable of achieving high quality material, that polycrystalline material is equivalent in optical quality to single crystal material, and that at least for  $\text{CaF}_2$ , purified "reagent" grade powder is equivalent to single crystal chips when used as starting material.

\* The bulk absorption coefficient is defined as the total absorption per unit length less the correction for surface loss, as determined from the slope and intercept (zero length), respectively, of the absorption versus length plots. An apparent absorption coefficient is defined as the total absorption per unit length with no surface loss correction.

Fig. 12  $5.25\mu\text{m}$  Optical Absorption vs Length for Cast  $\text{CaF}_2$

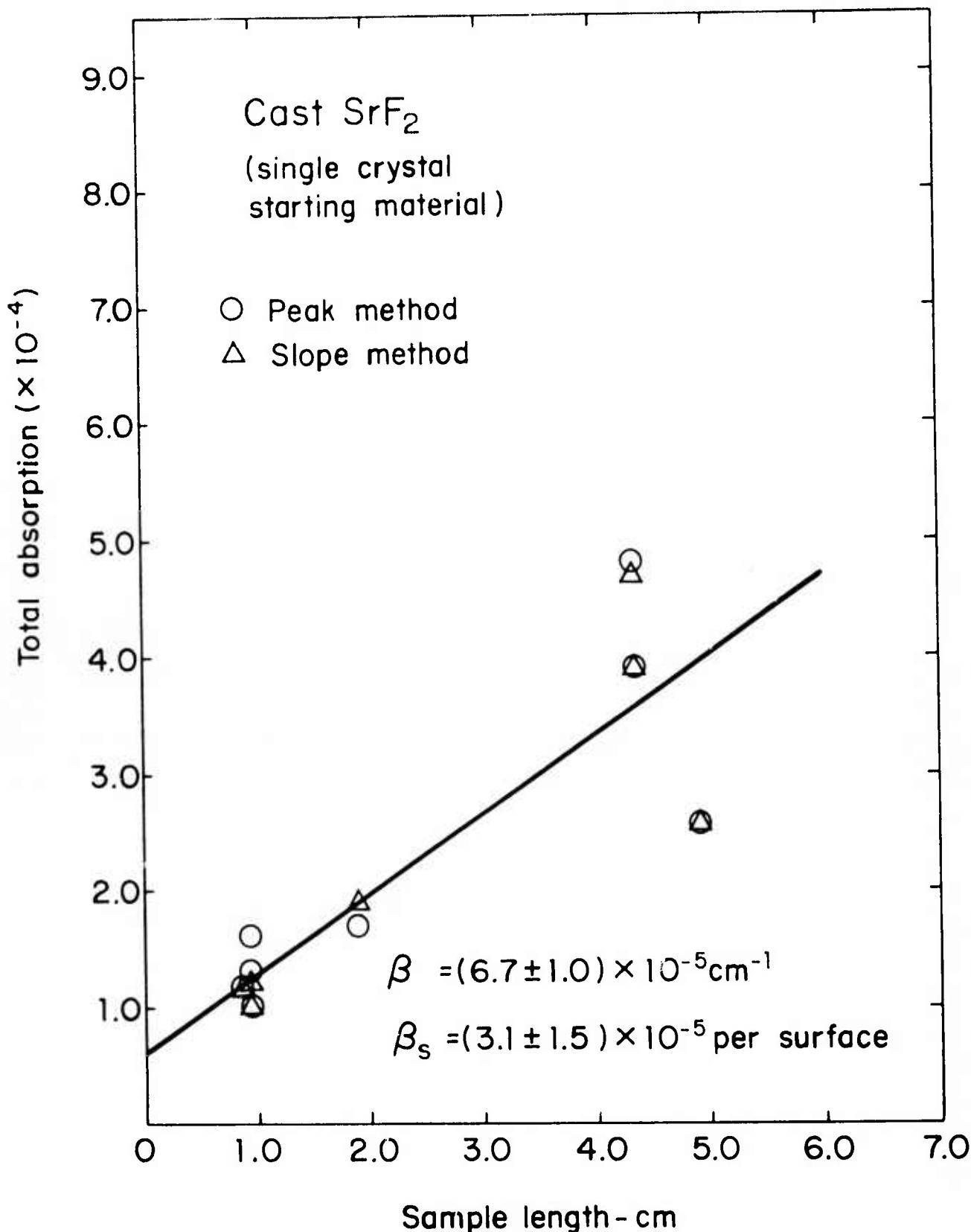


Fig. 13  $5.25\mu\text{m}$  Optical Absorption vs Length for Cast  $\text{SrF}_2$ .  
Harshaw single crystal chip starting material

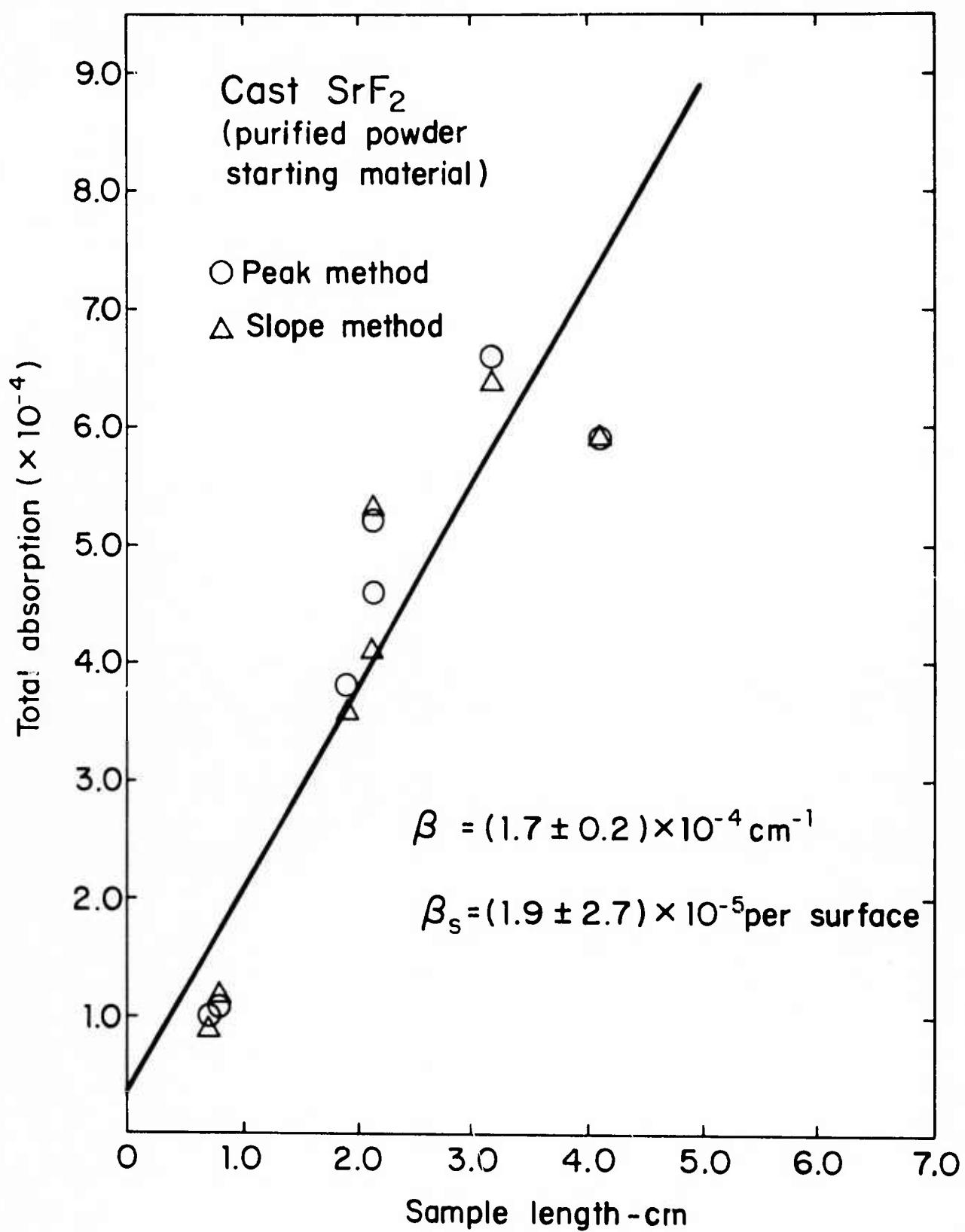


Fig. 14  $5.25\mu\text{m}$  Optical Absorption vs Length for Cast  $\text{SrF}_2$ .  
Purified "reagent" grade powder starting material

TABLE IX  
SUMMARY OF FLUORIDE MEASUREMENTS

<u>Material</u>	<u>Starting Material</u>	<u><math>\beta</math> Measured 5.25<math>\mu</math>m</u>	<u>Surface Correction</u>	<u><math>\beta</math> Predicted Exponential Law</u>
Optovac CaF <sub>2</sub>	--	(4.7 ± 0.3) × 10 <sup>-4</sup> cm <sup>-1</sup>	No	1.8 × 10 <sup>-4</sup> cm <sup>-1</sup>
Cast CaF <sub>2</sub>	Single crystal or purified powder	(4.2 ± 0.1) × 10 <sup>-4</sup>	(1.4 ± 0.8) × 10 <sup>-5</sup> per surface	
Harshaw SrF <sub>2</sub>	--	(4.1 ± 0.7) × 10 <sup>-5</sup> <sup>*</sup>	(3.9 ± 0.9) × 10 <sup>-5</sup>	2 × 10 <sup>-5</sup>
Cast SrF <sub>2</sub>	Single crystal	(6.7 ± 1.0) × 10 <sup>-5</sup>	(3.1 ± 1.5) × 10 <sup>-5</sup>	
Cast SrF <sub>2</sub>	Purified powder	(1.7 ± 0.2) × 10 <sup>-4</sup>	(1.9 ± 2.7) × 10 <sup>-5</sup>	

\* From reference 2.

Laser calorimetry measurements at  $3.8\mu\text{m}$  (DF laser) have been made by other investigators on several samples of Raytheon-cast material and indicate excellent quality. An apparent absorption coefficient at  $3.8\mu\text{m}$  for cast  $\text{CaF}_2$  was measured to lie near  $3.5 \times 10^{-4} \text{ cm}^{-1}$  at TRW.<sup>3</sup> At the University of Alabama, Huntsville,  $3.8\mu\text{m}$  apparent absorption coefficients were measured near  $6 \times 10^{-4} \text{ cm}^{-1}$ <sup>(4)</sup> and  $2 \times 10^{-4} \text{ cm}^{-1}$ <sup>(5)</sup> for cast  $\text{CaF}_2$  and cast  $\text{SrF}_2$ , respectively. No surface loss corrections were made on these above values.

For the samples of  $\text{CaF}_2$  single crystals heat treated in the Lindberg box furnace, the results are as follows: For the samples annealed in purified argon at either 800 or  $900^\circ\text{C}$  (sufficiently purged), no increase in the  $5.25\mu\text{m}$  apparent absorption coefficient ( $4.7 \pm 0.3 \times 10^{-4} \text{ cm}^{-1}$ ) was measured as compared to unannealed single crystal  $\text{CaF}_2$ . At  $1000^\circ\text{C}$  (in argon) an increase is observed ( $1.2 \times 10^{-3} \text{ cm}^{-1}$ ) with a corresponding increase in scattering (as viewed with a He-Ne laser). These results correlate with those reported earlier on vacuum ( $10^{-2} - 10^{-3}$  torr) annealing at 800, 900 and  $1000^\circ\text{C}$ .<sup>1</sup> In both cases it now seems clear that the systems are not sufficiently  $\text{O}_2$ -free, but that the damaging reactions occur only above  $900^\circ\text{C}$ , at least within the time period of these runs (10 hours) and with the low but unknown impurity concentration present.

For those samples of  $\text{CaF}_2$  cast with a partial pressure of argon (inert atmosphere of 1 - 50 torr) present, the samples were typically discolored as mentioned previously. One sample (VHP-318) that was discolored a faint yellow-blue had a measured  $5.25\mu\text{m}$  apparent absorption coefficient of  $5.8 \times 10^{-3} \text{ cm}^{-1}$ ; another similarly cast sample (VHP-317 - 50 torr argon) was colorless with a very good apparent absorption coefficient of  $4.1 \times 10^{-4} \text{ cm}^{-1}$ . However, another colorless sample (VHP-301 - 25 torr argon) was higher, with a value of  $1.16 \pm 1.2 \times 10^{-3} \text{ cm}^{-1}$ . However, for the latter value the loss may be surface connected. After repolishing by an optician the value fell to  $8.2 \pm 0.1 \times 10^{-4} \text{ cm}^{-1}$ , and with an additional chemical etch the value was  $6.7 \pm 0.6 \times 10^{-4} \text{ cm}^{-1}$ . Clearly, the above results are mixed and further work is underway to improve the technique.

## 2.6 Mechanical Properties

Preliminary mechanical property measurements have been obtained on  $\text{CaF}_2$  and  $\text{SrF}_2$ . Fracture strength as a function of surface preparation was determined for single crystal  $\text{CaF}_2$  and  $\text{SrF}_2$  and polycrystalline cast  $\text{CaF}_2$  and  $\text{SrF}_2$ . The stress strain curves were determined in three-point bending on an Instron universal testing machine. The sample span was one inch and the cross-head speed was 0.05 cm/min. Nominal sample cross sections were  $3/16 \times 3/16$  inches. Test bars were obtained from annealed ingots by cutting and polishing and were tested immediately or were either chemically polished in concentrated  $\text{H}_2\text{SO}_4$  or annealed prior to testing. For a number of samples extra attention was given to polishing the edge bevels, as noted in the tabulated results. Sample dimensions were measured after testing to prevent surface damage. Grain size for the polycrystalline cast samples is generally on the order of one cm. In all cases fracture occurred with no apparent yielding.

The results as presented in Tables X and XI show the effects of polishing and annealing on the fracture strength of  $\text{CaF}_2$ , and indicate qualitatively the large effect surface preparation has. By going from a rough polish (wet 600 grit grinding paper - Fig. 15) to a normal in-house laboratory polish (Fig. 16) or to an optical polish (polished on a pitch lap by an optician) as shown in Fig. 17, the strength of cast  $\text{CaF}_2$  is raised from 8000 psi to 14,600 psi and 13,900 psi, respectively. Moreover, the normal lab polished samples which were chemically polished prior to testing (calculated to remove about  $1 \times 10^5 \text{ \AA}$  from each surface) show a value of  $12,500 \pm 1800$  psi. Note that for the samples on which extra attention was paid to polishing the edge bevels, the fracture strength is raised to an average of 18,000 psi but decreased to 11,700 psi for the lab and optical polishes, respectively.

For single crystal  $\text{CaF}_2$  (Table XI) the polishing results are similar, i.e., going from a rough polish to lab and optical polishes, the fracture strength is increased from 7200 psi to 18,500 psi and 18,400 psi, respectively, values essentially equivalent to the cast material and not unexpected due to the large grain size of the castings.

TABLE X

FRACTURE STRENGTH OF CAST  $\text{CaF}_2$ 

As-Polished				As-Annealed			
Rough (psi)	Lab (psi)	Lab Edges (psi)	Optical (psi)	Optical Edges (psi)	Rough (psi)	Lab (psi)	Optical Edges (psi)
6200	9500	12300	14900	7600	9600	10900	27000
7700	7900	18100	11900	13300	13800	20600	16100
5700	8300	24100	14500	17600	17000	17500	16800
8500	22800	19700	15400	8200	8900	19600	20500
5000	20700	19800	13300	11400	11700	22000	26400
6900	7800	13800	10800	11900	15300	5400	6700
2000	14700	19500			24100		24200
24000	19100		18600		11500		21600
6400	20800		11100		18600		
8000	14600	18000	13900	11700	12700	16700	18900
±5900	±6000	±3900	±4300	±3300	±2900	±5800	±6900

\* 10 hours at 900°C in  $10^{-2} - 10^{-3}$  torr vacuum.

\*\* Extra attention paid to polishing the edge bevels.

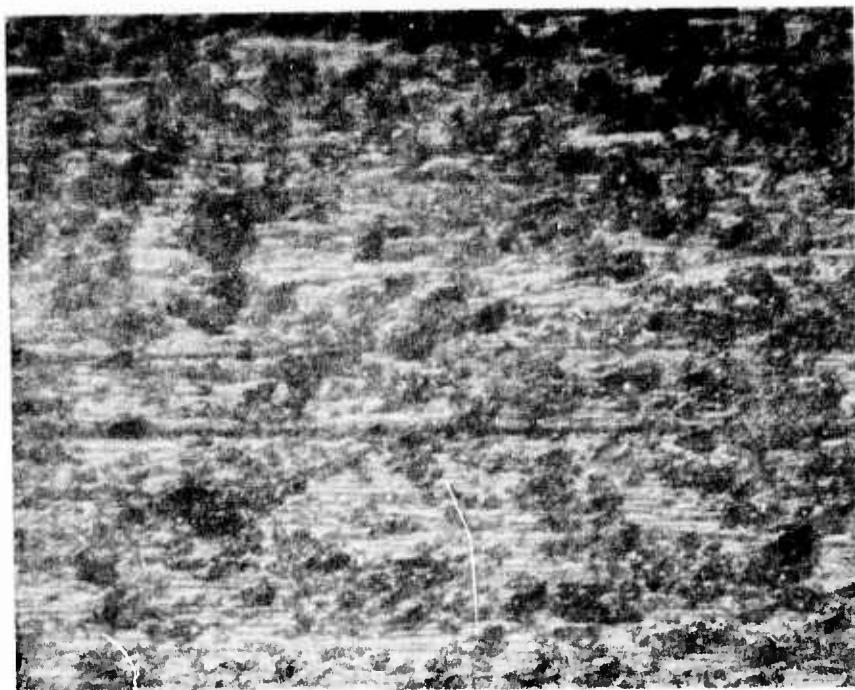
TABLE XI

FRACTURE STRENGTH OF SINGLE CRYSTAL  $\text{CaF}_2$ 

As-Polished		As-Annealed*	
Rough (psi)	Lab (psi)	Optical (psi)	Rough (psi)
2900	30800	15400	13200
5700	26600	12500	16700
3000	21800	15700	17000
2600	23200	17500	22500
8100	22000	28500	22800
52	14200	7800	20600
	9700		4800
	11400		10700
			27500
			23500
			3400
			7600
			7600
7200	18500	18400	15600
$\pm 4100$	$\pm 6600$	$\pm 5100$	$\pm 1700$

\* Annealed 10 hrs. at  $900^\circ\text{C}$  in  $10^{-2} - 10^{-3}$  torr vacuum.

\*\* Annealed 7 hrs. at  $1075^\circ\text{C}$  in  $10^{-5}$  torr vacuum.



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Fig. 15 Surface of CaF<sub>2</sub> Sample After Rough Polish (600 grit SiC Paper)  
187 X

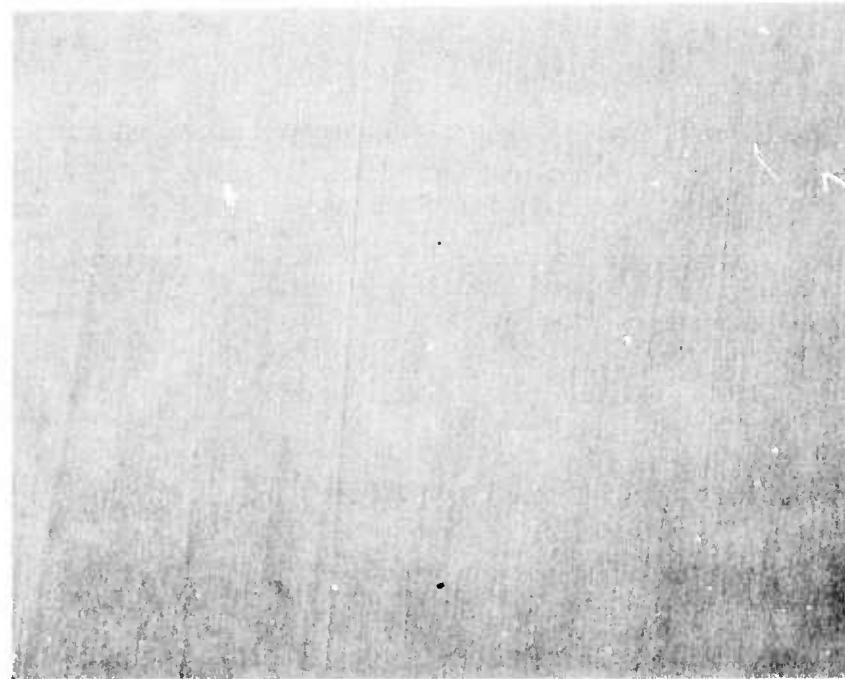


Fig. 16 Surface of CaF<sub>2</sub> Sample After Laboratory Polish. 187 X

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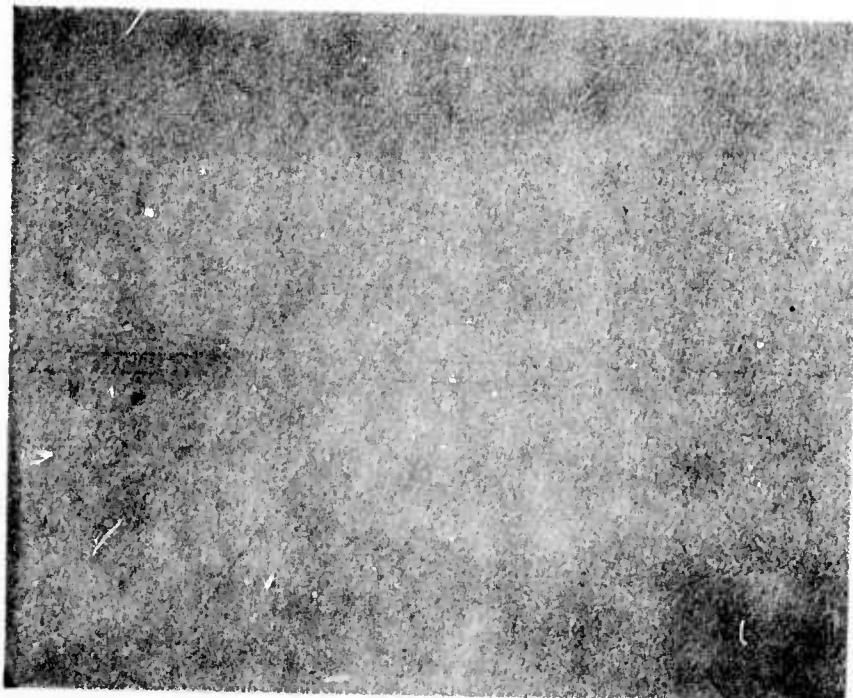


Fig. 17 Surface of CaF<sub>2</sub> Sample After Optical Polish (Pitch Lap). 187 $\times$

These polishing results (and the large scatter in the data) for both cast and single crystal material indicate that strength is limited by surface and edge flaws. Damaging flaws may be removed in part by more careful mechanical polishing.

Further evidence is seen in the effect of annealing individual test bars prior to testing as also indicated in Tables X and XI. Annealing significantly increases the fracture strength of both cast and single crystal specimens. Samples similarly polished as above - rough, lab, and optical polishes - and annealed prior to testing show increased fracture strengths of 12,700, 16,700, and 28,200 psi, respectively, for cast  $\text{CaF}_2$  and 15,600, 17,800, and 26,500 psi, respectively, for single crystal  $\text{CaF}_2$ . As was the case for as-polished cast samples, those as-annealed test bars on which extra attention was paid to polishing the edge bevels, the fracture strength is raised (to 18,900 psi) and lowered (to 23,400 psi) for the lab and optical polishes, respectively.

Evidently by annealing the test bars, some surface damage is either reduced or removed, a further indication that the fracture strength of  $\text{CaF}_2$  is limited by surface flaws. This assumes that bulk strain in all the bars are the same, supported qualitatively by viewing each specimen between crossed polarizers before testing and noting no differences. That is, all test bars appear macroscopically strain-free, whether they are to be tested as-polished or as-annealed (polished then subsequently annealed).

In all the above cases, fracture was predominantly transgranular in nature (i. e., cleavage). However, in the cases of samples of cast  $\text{CaF}_2$  which were taken from castings annealed in the degrading anneal procedure<sup>1</sup> (1000°C in vacuum of  $10^{-2}$  -  $10^{-3}$  torr) fracture was totally intergranular in nature and strengths were markedly reduced to  $4700 \pm 600$  psi (lab polished samples) from 14,600 psi. However, even in this instance, surface damage is limiting, since similar samples which were subsequently chemically polished show an increased strength to  $6500 \pm 1300$  psi, but still far below the 12,500 psi level of similarly chemically polished specimens cut from castings annealed at 900°C. Thus it appears that annealing procedure not only degrades the optical

properties<sup>1</sup> but also significantly affects the mechanical properties. Since fracture is intergranular, it suggests grain boundary weakening as a result of an impurity precipitation problem as previously discussed.

Preliminary results for single crystal and cast  $\text{SrF}_2$  samples as listed in Table XII show a surface damage dependence similar to  $\text{CaF}_2$ , although rough polished  $\text{SrF}_2$  is stronger than similarly polished  $\text{CaF}_2$ . For cast  $\text{SrF}_2$  the as-polished samples (rough, lab, and lab edge polishes) show average fracture strengths of 10,800, 11,200, and 12,800 psi, respectively. Similarly polished samples annealed prior to testing show an increased strength to 15,000, 16,000, and 16,200, respectively. Single crystal  $\text{SrF}_2$  shows an equivalent fracture strength compared to cast samples, i.e., the values for lab polished single crystal  $\text{SrF}_2$  are 11,300 psi and 16,400 psi for as-polished and as-annealed samples, respectively.

Hardness measurements were also taken on samples of  $\text{CaF}_2$  and  $\text{SrF}_2$ . Hardness is determined with a Vickers DPH indenter and a 50 gm load mounted on a Vickers M-55 metallograph. The results that appear in Table XIII show that there is no difference in hardness in single crystal or cast material for either  $\text{SrF}_2$  or  $\text{CaF}_2$  and that  $\text{CaF}_2$  is slightly harder than  $\text{SrF}_2$ .

TABLE XII

FRACTURE STRENGTH OF  $\text{SrF}_2$ 

As - Polished

As - Annealed

Cast $\text{SrF}_2$		S. C. $\text{SrF}_2$		Cast $\text{SrF}_2$		S. C. $\text{SrF}_2$	
Rough (psi)	Lab (psi)	Lab Edges (psi)	Lab (psi)	Rough (psi)	Lab (psi)	Lab Edges (psi)	Lab (psi)
10200	6500	11400	11800	17100	14500	14100	7700
10900	12200	6800	16100	14300	20900	18000	18900
11400	17700	8300	12500	13600	16700	14900	23400
	7900	15300	4800		11300	25600	15700
	7500		6200		21200	9400	
	19500		17700			9400	15100
	6400		22900			25400	
	8300		5800			5000	
	14600		11300			19900	
			24400			9100	
				14800			
					15000	16000	16400
					±1500	±6500	±5700

\* Annealed 10 hrs. at 900°C in  $10^{-2}$  -  $10^{-3}$  torr vacuum.

TABLE XIII  
VICKERS HARDNESS\* OF  $\text{CaF}_2$  AND  $\text{SrF}_2$

	<u><math>\text{SrF}_2</math></u>	<u><math>\text{CaF}_2</math></u>
Single Crystal	$171 \pm 2$	$191 \pm 2$
Polycrystalline Cast	$173 \pm 1$	$194 \pm 2$

\* Vickers Hardness Number, 50 gram load; average of four measurements.

### 3.0 SUMMARY AND CONCLUSIONS

#### 3.1 Casting

Consistently high quality castings of both  $\text{CaF}_2$  and  $\text{SrF}_2$  have been fabricated regardless of the starting materials. That is, either high purity single crystal chips or pre-treated (vacuum baked or RAP-reactive atmosphere processing - treated in teflon vapors) "reagent" grade powder can be used as starting material to yield equivalent castings.

Castings of  $\text{CaF}_2$  were attempted in an inert atmosphere - partial pressures of argon from 1 - 50 torr. The advantage is that unidirectional solidification is better accomplished because of the better heat transfer provided by the gas. The procedure needs more refinement because the castings are typically discolored.

#### 3.2 Hot Forging

Preliminary hot forgings of polycrystalline cast  $\text{CaF}_2$  have been done at  $1000^\circ\text{C}$ . At this high temperature a large grain size results so that not much advantage in grain size reduction is gained.

#### 3.3 Optical Properties

$5.25\mu\text{m}$  calorimetric bulk absorption coefficients of cast  $\text{CaF}_2$  have been consistently obtained near  $4.2 \times 10^{-4} \text{ cm}^{-1}$  regardless of the starting material. Those castings of  $\text{CaF}_2$  fabricated in an inert atmosphere of argon have  $5.25\mu\text{m}$  apparent absorption coefficients typically greater than  $1.0 \times 10^{-3} \text{ cm}^{-1}$ , although one was as low as  $4.1 \times 10^{-4} \text{ cm}^{-1}$ .

In preliminary results the  $5.25\mu\text{m}$  bulk absorption coefficient of cast  $\text{SrF}_2$  lies near  $6.7 \times 10^{-5} \text{ cm}^{-1}$  for an ingot cast using single crystal chips as starting material and lies near  $1.7 \times 10^{-4} \text{ cm}^{-1}$  for an ingot cast from purified "reagent" grade powder.

### 3.4 Strain Annealing

For highly strained ingots of cast  $\text{CaF}_2$  strain annealing has been successful at  $900^\circ\text{C}$  either in vacuum or inert atmosphere furnaces. Highly strained ingots of cast  $\text{SrF}_2$  have been successfully strained annealed at  $1000^\circ\text{C}$  in a high vacuum furnace.

### 3.5 Mechanical Properties

Mechanical measurements on cast  $\text{CaF}_2$  show average fracture strengths ranging from a minimum near 8000 psi to near 28,200 psi, depending on both the quality of polished surfaces (and edges) and whether or not the polished test bars are subsequently annealed at  $900^\circ\text{C}$  (a strain relief procedure). The results are equivalent to the values for single crystal  $\text{CaF}_2$  for which similar polishing and annealing procedures show average fracture strengths ranging from 7200 psi to 26,500 psi. In preliminary results the average fracture strengths for cast and single crystal  $\text{SrF}_2$  range from 10,800 psi to 16,000 psi and from 11,300 psi to 16,400 psi, respectively. The best (for  $\text{CaF}_2$ ) surface polish has not yet been evaluated for  $\text{SrF}_2$ . The dependence of fracture strength on both surface polish and annealing history is evidence that fracture for the fluorides is determined by surface and/or edge flaws. The preliminary results also show that  $\text{SrF}_2$  is equivalent in strength to  $\text{CaF}_2$  and that polycrystalline cast material is equivalent to single crystal material.

#### 4.0 PLANS FOR NEXT QUARTER

Work during the fifth quarter will include the following areas of effort:

1. Continue the investigation of purification treatments of "reagent" grade starting powder for fluoride castings, especially for  $\text{SrF}_2$ .
2. Continue the development of a casting procedure in an inert atmosphere.
3. Continue the mechanical property evaluation of cast fluorides ( $\text{SrF}_2$  and  $\text{CaF}_2$ ), including chemical-mechanical polishing procedures. Begin fractography analysis in order to determine points of fracture initiation in the fluorides.
4. Continue the evaluation of different annealing procedures, especially inert atmosphere operations at lower temperatures and teflon vapor operations at higher temperatures.
5. Investigate the effect of aliovalent additions to the fluorides under controlled casting conditions.

## 5.0 REFERENCES

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